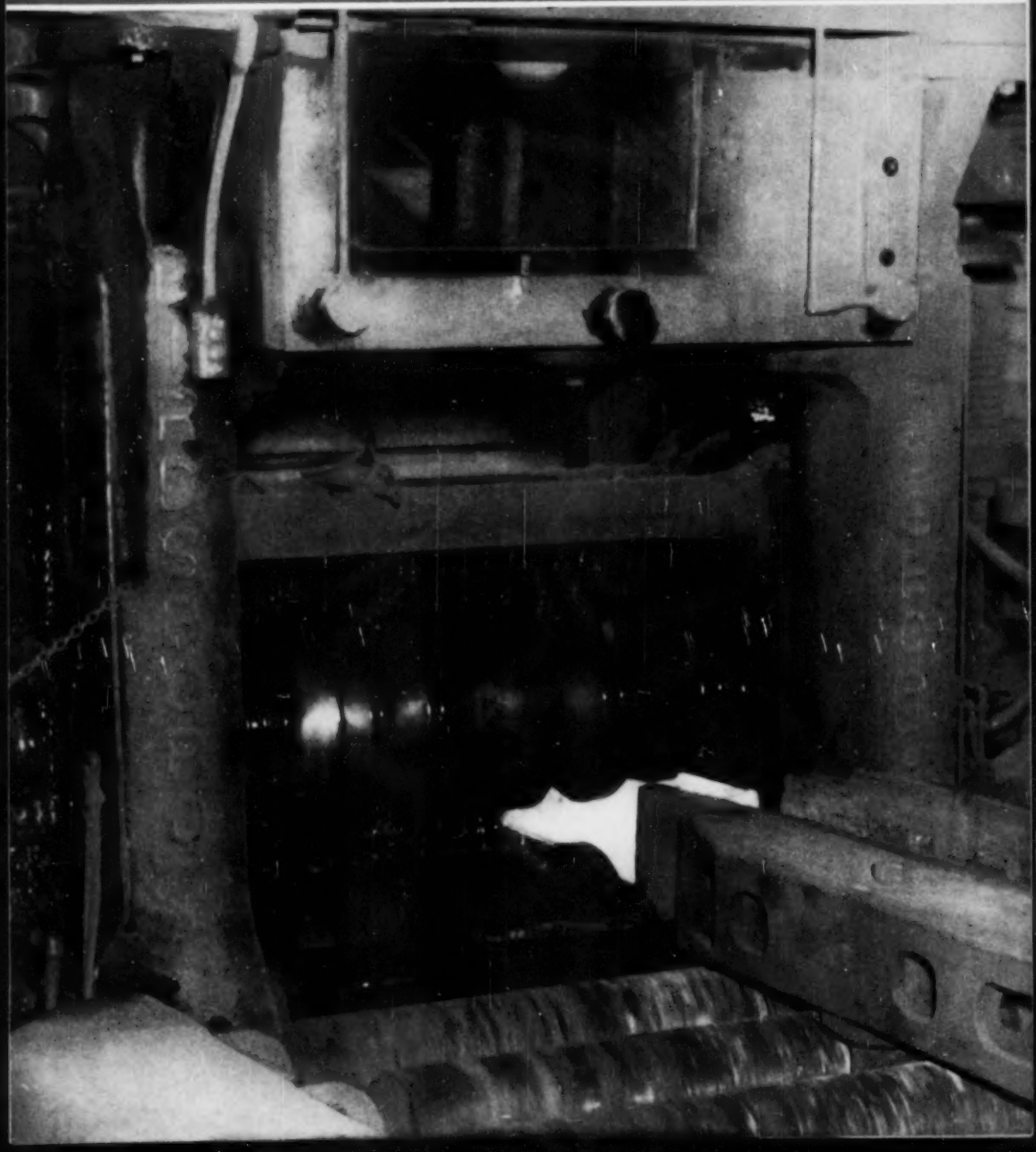
JULY, 1951

Journal of METALS



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Journal of METALS

Published to provide a continuing, authoritative, and up-to-date record of technological, engineering, and economic progress in all branches of the metals industry by the

Metals Branch

American Institute of Mining and Metallurgical Engineers, Inc.
29 West 39th Street, New York 18

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The AIME Publishes:
Journal of Metals
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VOL. 3, NO. 7 — JULY, 1951

COVER

A half-ton Ti 150A high-strength titanium alloy ingot is shown being bloomed to forging bar size at Watervliet, N. Y., for Titanium Metals Corp., a company owned jointly by National Lead Co. and Allegheny Ludlum Steel Corp. This is believed to be the largest ingot in regular production. This particular alloy is used extensively for forged disks and blades for compressor sections in some of the new jet power units.

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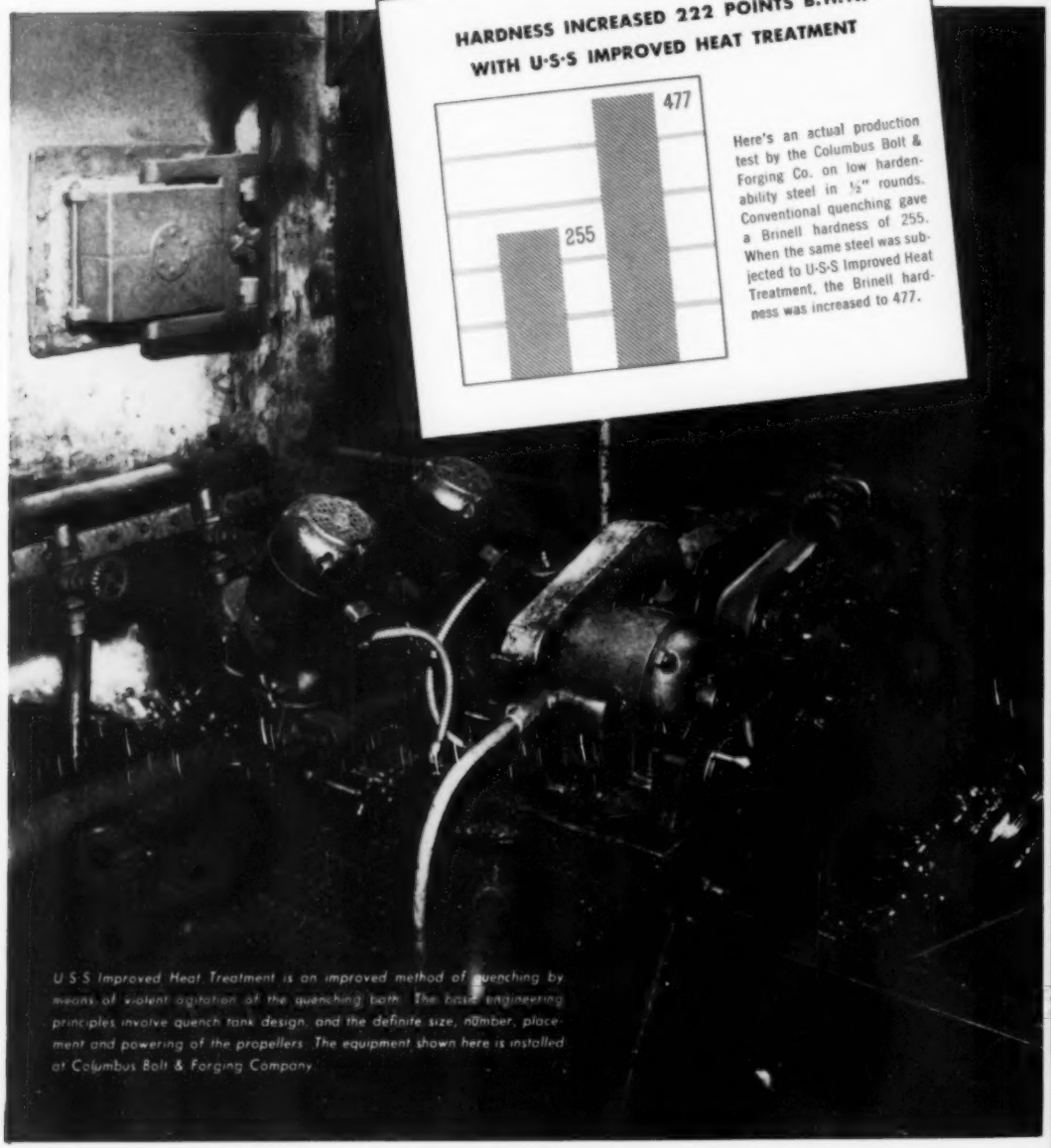
HARDNESS INCREASED 222 POINTS B.H.N.
WITH U·S·S IMPROVED HEAT TREATMENT
255
477
Here's an actual production test by the Columbus Bolt & Forging Co. on low hardenability steel in ½" rounds. Conventional quenching gave a Brinell hardness of 255. When the same steel was subjected to U-S-S Improved Heat Treatment, the Brinell hardness was increased to 477.

U·S·S Improved Heat Treatment is an improved method of quenching by means of violent agitation of the quenching bath. The basic engineering principles involve quench tank design, and the definite size, number, placement and powering of the propellers. The equipment shown here is installed at Columbus Bolt & Forging Company.

THE ALLOY STEEL YOU'RE GETTING

on quenching methods

TODAY, as critical alloying elements become scarce, all users of alloy steel are faced with the necessity of getting the most out of the steel they're receiving.

In most cases, this puts the problem squarely up to the heat-treater. Better heat-treatment methods can often do the job.

If you encounter difficulties, don't be too quick to blame the steel or the heating practice. The answer may be better *quenching* methods. More specifically, your problem might be solved with U·S·S Improved Heat Treatment — a superior quenching technique developed by United States Steel.

U·S·S Improved Heat Treatment extracts heat rapidly and *evenly* from every part of the material's surface. This treatment assures accurate timing, allowing removal of the material from the quenching bath while a certain amount of residual heat is present. Elapsed time from quench to tempering treatment is held to an absolute minimum. This not only improves mechanical properties; it also reduces cracking. And, this quenching method improves machinability by minimizing the formation of free ferrite in hypo-eutectoid steels.

The use of this quenching process is available to you without charge.

United States Steel does not manufacture or sell heat-treating equipment, but our metallurgists will be glad to analyze your heat-treating methods and make suggestions that may give you more uniform hardness, less rejects and less retreatment.

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UNITED STATES STEEL EXPORT COMPANY, NEW YORK

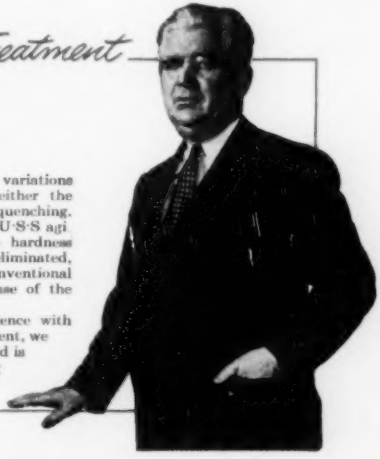
Comments on U·S·S Improved Heat Treatment

by Mr. R. E. Christin, Chief Metallurgist
Columbus Bolt & Forging Co., Columbus, Ohio

"Quenching is a process often neglected in heat treatment. We feel it is just as important (if not *more* important) than any other phase of heat treatment. There is a tendency to concentrate too much on the heating—and lay too much blame for failure to the heating—when proper quenching could produce the objectives desired. Heating, even in the ideal environment, can be inadequate if quenching is faulty.

"Before we installed U·S·S Improved Heat Treatment, we occasionally encountered hardness variations in the as-quenched condition. These variations were loosely attributed to either the steel, or the heating or the quenching. However, after adopting the U·S·S agitated quench process, these hardness variations were practically eliminated, obviously indicating that conventional quenching was the chief cause of the hardness variations.

"After seven years' experience with U·S·S Improved Heat Treatment, we are convinced that this method is the answer to most hardening problems."



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2—ABRASION RESISTING LINING: Cast Basalt, a natural volcanic rock, is said to offer long life when used for lining ash races, bunkers, chutes, hoppers, cyclones, etc. The material comes in the form of flat or curved tiles, and is acid resistant. *H. Windsor & Co. Ltd.*

3—RUST INHIBITOR: A scientific boiler and metal protector, Corrosanti is manufactured in four grades by *Dr. Adolph Shror* for the protection of boiler metal surfaces, ferrous metals, water tanks, underground piping, smokestacks, flues, etc.

4—STARTING UNIT: The combination Life-Line-starter available from *Westinghouse Electric Corp.* offers improved starting and control of machine tools, presses, and other equipment. The unit comes in NEMA sizes 1 to 5, with ratings up to 200 hp, 440 v polyphase.

5—DECALS: Mar-proof and fungus-proof decals, specially designed for high resistance to abrasion, moisture, and temperature extremes are offered by *Meyercord Co.* These decals, which are unaffected by acid, alkali, alcohol, or petroleum products, have been used as wiring diagrams, instruction signs, insignia, and nameplates.

6—NESTING SKIDS: All steel, welded nesting skids, manufactured by *Bloom System, Inc.* and designed for use with all types of floor trucks, are said to permit more efficient use of floor space and result in added handling capacity for the movement of materials and stock.

7—RECORDING INSTRUMENTS: Recording voltmeters and ammeters that make a continuous record on an 8-in. circular chart, feature a new moving-iron measuring mechanism that produces a high actuating torque at low electrical burden. *The Bristol Co.*

8—ROLLING MILL: An integrated versatile mill, manufactured by *United Engineering & Foundry Co.*, is designed for cold rolling copper, brass, aluminum, carbon and stainless alloy steel strip, down to 0.002 to 0.004 in. at speeds of 500 to 2000 fpm. Each packaged unit is furnished fully equipped.

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July

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Free Literature

20—METALLOGRAPH: A 20-p. catalog describing the Balphot Metallograph with its four types of illumination and Magna-Viewer projection screen is offered by *Bausch & Lomb Optical Co.*

21—BURNERS FOR GAS AND OIL: Small capacity, long flame burners for gas, oil, or gas and oil, are described in a 16-p. booklet available from *Bloom Engineering Co., Inc.*

22—METALLOGRAPHIC POLISHING: Two-speed specimen polishing units, described in a booklet by *Buehler Ltd.*, are available for flush or table mounting.

23—HIGH TEMPERATURE INSULATION: Information on *Illinois Clay Products Co.* insulation and refractories for furnaces, soaking pits, and coke ovens is contained in a new folder.

24—VANADIUM STEELS: Metallurgists and design engineers are offered a book giving composition, heat treatments, mechanical properties, and uses for 180 different vanadium irons and steels for all applications. *Vanadium Corp. of America.*

25—MAGNETIC SEPARATORS: A 16-p. catalog on "Non-Electric Permanent Magnetic Separators for Tramp Iror Removal" is being issued by *Eriez Mfg. Co.* Descriptions of separators and pertinent engineering data are given.

26—CHART RECORDER: A bulletin concerning the Multipoint Capacilog strip chart recorder has been released by *Wheelco Instruments Co.*

27—TEST SPECIMENS: Common metals and alloys, mounted and identified, complete with photo-micrograph, analysis, hardness etc., for comparison or teaching, are described in a booklet of *Adolph I. Buehler.*

28—INSPECTION EQUIPMENT: A variety of optical and illuminating equipment including black and fluorescent lighting for inspection jobs is cataloged in a bulletin of *Arthur S. La Pine & Co.*

29—RESEARCH LABORATORY: A 14-p. booklet detailing the aims and scope of research at one of its laboratories is offered by *Aluminum Corp. of America.*

30—MONOCHROMATIC COLORIMETER: A single-cell, direct reading, photo-electric colorimeter is described in a pamphlet by *Bausch & Lomb Optical Co.*

Coming Events

July 5-11, National Management Council, International Management Congress, Brussels, Belgium.

July 9-11, Idaho Mining Assn., annual convention, Sun Valley, Idaho.

July 30-Aug. 2, American Electroplaters' Society, Statler Hotel, Buffalo, N. Y.

Aug. 7, AIME, Morenci Sub-section, Longfellow Inn, Morenci, Ariz.

Aug. 27-Sept. 6, Oak Ridge National Laboratory and Oak Ridge Institute of Nuclear Studies, annual summer symposium, Oak Ridge, Tenn.

Sept. 13-15, AIME, Industrial Minerals Div., fall meeting, University of West Virginia, Morgantown, W. Va.

Sept. 16-19, American Institute of Chemical Engineers, regional meeting, Sheraton Hotel, Rochester, N. Y.

Sept. 19, AIME, Carlsbad, Potash Section, Riverside Country Club, Carlsbad, N. Mex.

Sept. 20, AIME, Utah Section, Newhouse Hotel, Salt Lake City.

Sept. 25-28, ASME, fall meeting, Radisson Hotel, Minneapolis.

Oct. 1-4, Assn. of Iron & Steel Engineers, annual convention, Hotel Sherman, Chicago.

Oct. 3-5, AIME, petroleum branch, fall meeting, Oklahoma City.

Oct. 9-12, Scientific Apparatus Makers Assn., mid-year meeting, Recorder-Controller Section, Seaview Country Club, Absecon, N. J.

Oct. 10-11, Joint Fuels Conference, AIME Coal Division, ASME Fuel Section, Roanoke Hotel, Roanoke, Va.

Oct. 10-11, AIME, Southwestern and Western Sections, Open Hearth Committee, joint meeting. Oct. 10, plant trip, Colorado Fuel & Iron Co., Pueblo. Oct. 11, Broadmoor Hotel, Colorado Springs.

Oct. 12, AIME, Eastern Section, Open Hearth Committee, Warwick Hotel, Philadelphia.

Oct. 12-14, Metal Treating Institute, annual meeting, Detroit.

Oct. 15-17, AIME, Institute of Metals Div., fall meeting, Detroit-Leland Hotel, Detroit.

Oct. 15-19, National Metal Congress & Exposition, Detroit.

Oct. 18-20, National Assn. of Corrosion Engineers, south central region, Corpus Christi, Texas.

Oct. 19-20, Engineers' Council for Professional Development, annual meeting, Hotel Statler, Boston.

Oct. 22, AIME, Chicago Section, Open Hearth Committee, Phil Schmidt's, Chicago.

Oct. 22-24, American Mining Congress, Metal and Nonmetallic Mining Convention, Biltmore Hotel, Los Angeles.

Oct. 22-27, Societe Francaise de Metallurgie, Congress, Paris, France.

Oct. 25-26, AIME, Los Angeles Section, fall meeting, Los Angeles.

Oct. 25-26, Credit Bureau of Circulation, annual meeting, Congress Hotel, Chicago.

Oct. 26-27, AIME, National Openhearth Committee, Southern Ohio Section, Deshler-Wallick Hotel, Columbus, Ohio.

Oct. 29-Nov. 3, AIME, fall meeting, Mexico City.

Nov. 2, AIME, Pittsburgh Local Section and Open Hearth Local Section, annual off-the-record meeting, William Penn Hotel, Pittsburgh.

Nov. 25-30, ASME, annual meeting, Chalfonte-Haddon Hall, Atlantic City.

Nov. 28-30, Scientific Apparatus Makers Assn., midyear meeting, industrial instrument, laboratory apparatus, laboratory equipment, optical, nautical, aeronautical, and military instrument sections, Hotel New Yorker, New York.

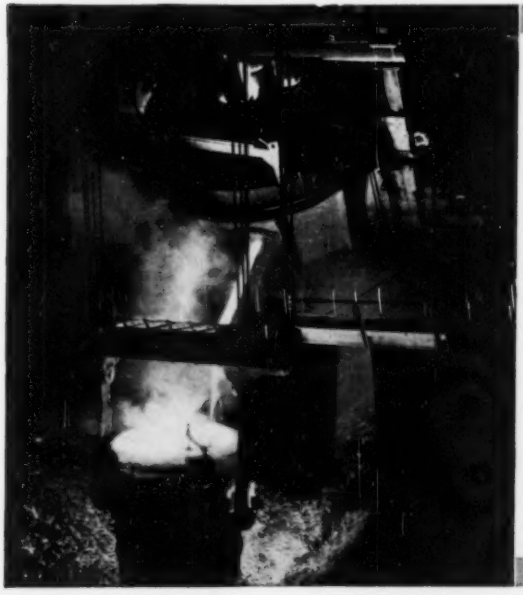
Nov. 29, AIME, Buffalo Section, Open Hearth Committee, Statler Hotel, Buffalo, N. Y.

Dec. 2-5, American Institute of Chemical Engineers, annual meeting, Chalfonte-Haddon Hall, Atlantic City.

Dec. 6-8, AIME, Electric Furnace Conference, William Penn Hotel, Pittsburgh.

Jan. 16-18, 1952, Society of Plastic Engineers, Inc., annual national technical conference, Edgewater Beach Hotel, Chicago.

Feb. 18-21, AIME, annual meeting, Hotel Statler, New York.



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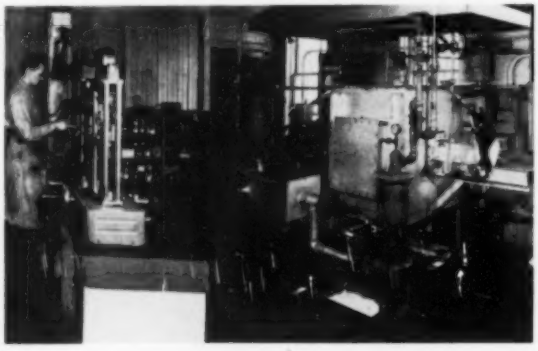
Junior Engineer, 26 to 30, metallurgical or mining graduate, with mining and milling equipment experience, to assist in office engineering covering correspondence, purchasing, specifications, expediting, etc. Occasional trips. Salary, $4200 to $4500 a year. Location, New York. Y5551.

Engineers. (a) Assistant to general manager, graduate, with considerable experience in management. Knowledge of Spanish desirable. (b) Metallurgical engineer, graduate, with considerable experience in milling and research, capable of directing operations of heavy medium and gravity plants, and in advisory capacity at other mills. Should be able to direct and carry on research in the beneficiation of tin ores in the experimental laboratory. (c) Superintendent of the sink and float plant, graduate, with 5 or more years' experience in milling. Should be mechanically inclined and have some experience as mill superintendent elsewhere. Should have working knowledge of Spanish and be able to handle Latin American labor. (d) Junior metallurgists, graduates, with some experience in milling practice as well as laboratory research. Location, South America. Y5549.

Metallurgist, position as mill superintendent for a copper company in New England. Y5542.

Production Manager, 40 to 50, with heavy machinery and sheet metal experience, to be responsible for production planning, assembly, etc. of metal products firm. Salary, $8000 to $10,000 a year. Location, Massachusetts. Y5474.



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Sales Engineer, about 30, mechanical graduate, with some sales experience, for sale of industrial oil to paper mills, automotive manufacturers, heavy industry, etc., for major oil company. Location, Wisconsin. Y5480.

Sales Engineer, recent graduate, interested in aircraft. Knowledge of sheet metal forming, or experience on heavy press equipment. Intermittent traveling to nearby states. Salary, $3900 to $5200 a year. Location, New York. Y5457.

Metallurgist, to 35, B.S. in metallurgy or metallurgical engineering, recent graduate to several years' experience. General metallurgical work and X-ray analysis on both ferrous and nonferrous metals. Opportunity to work with an experienced metallurgist on numerous and varied problems inherent in a modern welding research laboratory. Salary, $3600 to $5100 a year. Location, northern New Jersey. Y5416(b).

Forging Engineer, over 40, with considerable experience in forging production and at least 10 years' production management experience. Work involves out of town assignments at least 50 pct of time. Salary, $7600 a year. Headquarters, Washington, D. C. Y5412.

Metallurgist, 7 to 10 years' experience in supervisory capacity in aluminum, alloy and stainless steels, and metallurgical work, preferably with high temperature applications. Knowledge of shop operations and metallurgical laboratory. Good knowledge of aircraft engines would be helpful as applicant will establish and operate metallurgical laboratory for manufacturer of aircraft engines. Salary open. Location, Indiana. T7809.

Superintendent, iron ore concentration plant. Must have 5 or more years' experience in supervising mineral beneficiation plants, and knowledge of modern ore-dressing processes and equipment. Will supervise operation of large, modern iron ore concentrator. Salary open. Location, Minnesota. T7759.

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Mineral Economist, 28, married, B.S. mineral economics and geology, Penn State College; M.A. resources and economics, University of Texas. Experienced coal mining, concentrating plants and manufacturing of copper products. Desires responsible position mining or iron and steel industry in sales engineering or other specialized work relating to this field. M-624.

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Box F-7, JOURNAL OF METALS

Meet The Authors

H. S. CANNON

GUIDO BASSI

Guido Bassi (p. 533) was born in Monfalcone, Italy, and was awarded the degree of Dipl. Ing. in Leoben, Austria. He is now research engineer at AB Svenska Metallverken, Vasteras, Sweden. His hobbies are chess and tennis.

H. S. Cannon (p. 529) received his B.S. degree from Carnegie Institute of Technology, and his M.S. degree from Rensselaer Polytechnic Institute, where he is now a metallurgical fellow. A student associate of AIME, he belongs to ASM and Sigma Xi. Photography and his children occupy his spare time.

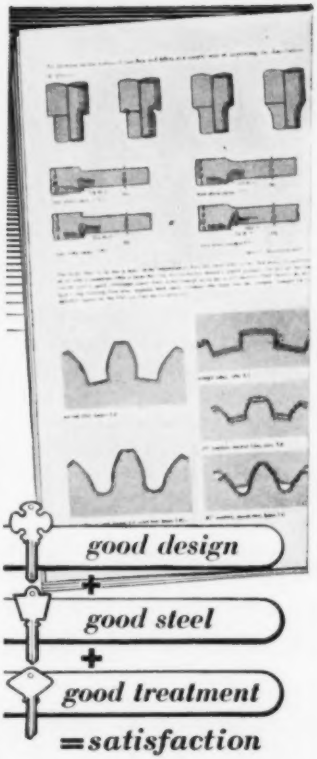
L. B. Gulbransen (p. 522) studied at Colorado School of Mines and University of Utah, receiving his B.S., M.S. and Ph.D. degrees. Now assistant professor of metallurgy at Colorado School of Mines, he belongs to ASM and Sigma Xi. He likes photography and model building.

D. C. Buffum (p. 540), a graduate of Tufts College, is physical metallurgist in the research laboratory of the Watertown Arsenal. A member of AIME and the American Crystallographic Assn., his hobby is photography.

J. H. Hamilton (p. 522) was awarded his Ph.D. degree at California Institute of Technology. Since 1944 he has been director of Utah Engineering Experimental Station, and professor of metallurgy at University of Utah. This member of AIME, AIEE, Sigma Xi, and Utah Soc. Professional Engineers likes golf and sports in general.

D. C. BUFFUM

L. B. GULBRANSEN



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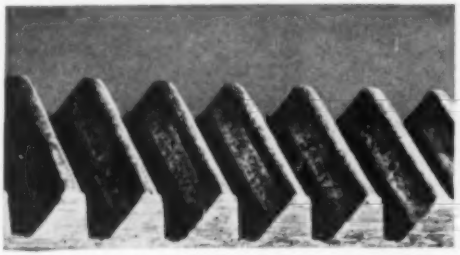
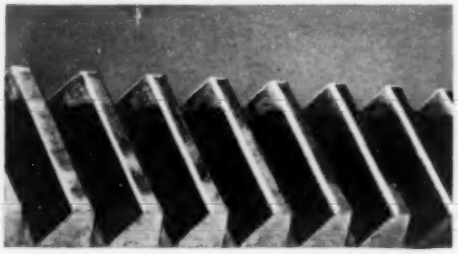


This forged steel gear rack shows severe wear and pitting. The rack was made from free-machining, medium carbon, resulfurized manganese steel, corresponding in composition approximately to the A.I.S.I. C-1137 type. It was used as-forged, with a hardness of 200 Brinell, to operate against a gear made from sintered high carbon steel, copper-impregnated, with a tensile strength of 85,000 p.s.i.



This ductile iron rack, produced by The Acme Shear Company, Bridgeport 1, Conn., showed no pitting . . . after exactly the same service test as the steel rack. The only evidence of wear is a burnished appearance on edges of the teeth. This ductile iron rack had a hardness of 205 Brinell, but any hardness within the range of 150/200 proves satisfactory under similar conditions. Saving in cost is estimated at 60%, based on the low initial cost of ductile iron, and its superior machinability.

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A plant for production of steel parts made by cold extrusion is being contemplated by a large manufacturer. The bulk of cold extrusions to date have been military items such as shell cases, projectiles, and missile parts, but greater interest is being expressed in the process by manufacturers of non-military items.

Demand for lithium and lithium compounds has expanded tremendously within the past couple of years so that now they are becoming quite difficult to obtain in spite of expanding production capacity. This increase in demand is partly the result of wide application of lithium compounds in low firing temperature frits for porcelain enameled products and in the manufacture of lubricating greases.

Crane Co. is the latest company to enter the titanium race. Plans call for ownership of all properties and facilities from mining of ores to actual metal production. Crane, one of the country's outstanding producers of various types of valves, will utilize titanium metal in valve production. Currently, the company is buying titanium tetrachloride from the Stauffer Chemical Co., Niagara Falls, and is making titanium by reaction with magnesium.

British motor car production is feeling the effects of restrictions in the use of steel, with present steel allocations running up to 20 pct less than individual companies were receiving in the last quarter of 1950. Allocations may improve toward the end of the year. Zinc scarcity, however, shows no sign of alleviation, and would have cut the industry's output this year by 10 to 15 pct without any shortage of steel.

Japan completed building 332,000 gross tons of ships during the production year Apr. 1, 1950 to Mar. 31, 1951, which was the record postwar year for the industry. Construction in 1949 totalled 140,000 tons. Main items included 32 freighters, 19 tankers, and 21 vessels for export.

A British commission has estimated the world sulphur shortage for 1951 will be about 1 million tons or 20 pct of the U. S. output and twice the British consumption during 1950. While American and Italian resources are becoming depleted rapidly, it is believed that there are unexploited reserves in New Zealand and Iceland.

GM's Cadillac Div., turning out the Walker Bulldog light-gun tank, has 1400 first line subcontractors in 24 states, who in turn subcontract with about 6000 other firms throughout the country.

Net gold sales by U. S. to other countries during first quarter of 1951 totalled $898 million. This amounts to about 16 pct more than sales during last quarter of 1950. Preliminary figures on sales during April 1951 show a decline to a quarterly rate of $78 million, less than 10 pct of the rate for the fourth quarter of 1950.

The Navy's new attack submarines will be powered by an outstanding new radial-type diesel engine that has been under development for five years. It is a 16-cylinder, 2-cycle diesel, vertically mounted with four rows of cylinders radially arranged. It is the lightest engine in its power range. Engines previously used are twice as heavy and half again as large. General Motor's Cleveland Diesel Div., builds them.

Drift of Things . . . . . as followed by **Edward H. Robie**

IN the employment situation for professional men in the mineral technology field, the pendulum seems to swing rapidly and far. Less than a year ago more men were seeking jobs than there were openings available. This was particularly true of young men and inexperienced college graduates. Just the reverse is now true. The Engineering Societies Personnel Service reports that it recently has been able to find men for only 7 pct of the openings that it has available. In more normal times the figure is 35 or 40 pct. Those who might be interested in considering another job, therefore, might find it to their advantage to register with the Personnel Service. Also, they would thereby make it possible for the Service to do a better job in filling requests from employers.

The Personnel Service has four offices. One should register with the office that serves the area in which a job would be most attractive. Registration with more than one office is permissible. Western mining and oil men would naturally clear through the San Francisco office; most metallurgists through one of the Eastern or Mid-Western offices. The addresses are: 8 W. 40th St., New York 18; 100 Farnsworth Ave., Detroit; 84 E. Randolph St., Chicago 1; and 57 Post St., San Francisco. There is no charge for registration—only if a job is secured. The fee for AIME members is one week's salary for jobs paying less than $3000 a year, ranging up to 3¾ pct of annual salary for jobs paying $5000 or more. A registrant is kept on the active list for 2 months. If a job is not obtained in that time, he may on request be kept on the active list longer. If a job is offered but not accepted there is no charge.

All jobs are coded, so no publicity is given to a registrant except to the potential employer to whom the registrant is referred and who has asked for a man with his type of experience.

Bargain for New Junior Members

Never before, we believe, have newly elected Junior Members of the AIME received such a bargain. Graduating Student Associates are being given a special incentive to change their status to Junior Membership, and young men out in the industry, not over 30 years old, who are not yet members will probably never have a better incentive to apply.

Beginning with elections in June 1951, all new Junior Members are privileged to receive a copy of the immensely popular reprint of "*Agricola*," some 2500 copies of which have been ordered by AIME members since the volume was issued early last December. The stock was soon exhausted but more are now available. This is a $10 book, with no discount permitted. The Institute, however, has purchased through money made available by the Seeley W. Mudd Memorial Fund 1400 copies for gratis distribution to new Junior Members. Also they automatically receive a copy of "*A Professional Guide for Junior Engineers*" and their choice of one of seven other volumes ranging in price from $1.50 to $5. If their interests happen to be in petroleum, they also receive a fourth free volume, listed at $2.50, on the legal aspects of the unit operation of oil pools. Thus, for the initial year's dues of $12, (there is no initiation fee) a Junior Member receives a year's subscription to the journal of his choice and up to $18.50 worth of books.

The opportunity to purchase books at special prices is an advantage that all members receive, but is not always realized. Books published by one of the Institute's Funds are available to members at approximately half the price that a commercial publisher would place on a similar book. Also, AIME members are granted a 10 pct discount on a wide variety of other publishers' books. For those who keep their libraries up to date and well stocked, the savings thus possible may well offset the annual dues.

Transactions Volumes

The AIME has a surplus stock of certain Transactions volumes issued prior to 1928 that it will sell at cutrate prices. Normally these sell at $5, less 30 pct to AIME members, for the leather-bound editions. Until Aug. 1, orders will be accepted for the available leather-bound copies at $2.25, and for the paper-bound copies at $1 each. The leather in many of these books is not in good condition, and the paper-bound volumes are discolored and soiled, so the books are sold "*as is*." If pages are found missing or the print is illegible, however, refund will be made.

Leather-bound volumes are available of all volumes from No. 2 to No. 76 inclusive except Nos. 5, 8, 9, 18, 64, 69, 72, and 73. Paper-bound copies are available of all except Nos. 5, 8, 9, 22, 28, 31, 37, 39, 41, 45, 50, 58, 62, 63, 67, 68, 74, and 76. Orders are subject to prior sale.

Here's a chance possibly to complete your library. Or merely to buy a book or two for a nominal price and see what the experts believed 25, 50, or 75 years ago.

Bless His Heart

It has been said that even when business is sound, the sound is mostly complaint. Human beings are much more likely to complain about something they do not like than to give thanks for what they do like. Most everybody seems to consider perfection a matter of course. So a normal number of expressions of dissatisfaction with the activities of any organization are to be expected. But something drastic should be done if the complaints are numerous or if they indicate remediable faults.

Complaint letters received by the AIME are by no means numerous, but occasionally a member does have just cause for resentment, and sometimes two or three just causes.

All of which is leading up to a letter we received on Apr. 23 from a petroleum engineer at the University of Texas—a Junior Member. "The purpose of this letter", he says, "is not to offer a sad tale of woe, nor to mention my 'sad neglect', but rather to express my sincere appreciation for a job well done. In the past I have found it comparatively easy to complain of a situation but more difficult to give credit where credit is due. So as not to fall into the category of a 'complainer', I want to take this opportunity to thank you for the manner in which you handled my letter of Apr. 6. It is my hope that the Institute will continue to have competent personnel in its offices to straighten out little mixups that will always occur in an organization as large as ours. Thanks a million—"

Needless to say the staff member who handled this particular transaction was set up no end when she received this praise. If she has her way, the young man who wrote this letter will have preferred treatment at Institute headquarters for a long time to come.

Sweden's Iron and Steel Industry

by T. L. Joseph

Scene at the Kiirunavaara Mine, Kiruna, Sweden.

During the summer of 1950 the author visited several large iron ore mines and steel plants in Sweden as a guest of Jernkontoret, an association of Swedish steel producers. His report on this old and efficiently managed industry covers iron ore, concentrating, sintering, iron production, steel production, and phases of these functions that were developed to meet conditions peculiar to the country.

LARGE reserves of dense magnetite, cheap electric power, the lack of domestic coking coal and the availability of charcoal have been dominant factors in shaping Sweden's iron and steel industry. To minimize the consumption of expensive domestic charcoal and imported coke, progress has been made in preparing burdens high in iron and low in silica that are easily reduced. Charcoal pig iron, used exclusively for producing quality steel and gray iron castings, still is produced in substantial tonnages. The capacities of individual furnaces are relatively small, and emphasis is on close control of the operation rather than on tonnage. Several small blast furnaces generally are preferred to a single large unit because the smaller units operate efficiently on self-fluxing sinter and produce iron of uniform analysis.

Sweden exports a large portion of its iron ore, particularly that which comes from the Kiirunavaara and Loussavaara mines at Kiruna and from mines in the Malmberget district. These mines, located well above the Arctic circle, are close to a main rail line that connects Narvik, Norway, with Lulea on the Baltic. Most of the ore from these mines is shipped through the Norwegian port of Narvik, which has an open harbor the year round. Production of iron ore, concentrates and sinter is shown in Fig. 1. From 1911 to 1925, about 6 million metric tons of ore and concentrates were produced annually. Output rose to about 9 million tons per year in the late 1920's; dropped to about 5 million in the early 1930's; then rose sharply to 13 million tons under the impact of European preparations for World War II. By 1945, production had decreased to about 4 million tons and exports were slightly over 1 million tons. Three years later, the prewar peak of about 13 million metric tons was exceeded. The curve for exports falls close to that for total production, showing that exports are normally about 85 pct of production.

The Kiruna ore is graded according to phosphorus content, which ranges from under 0.03 to 2.0 pct. Iron content ranges from 60 to 68 pct, with SiO_2 about 3 pct or less. Alumina and manganese are low with a range of several per cent of lime. High iron and low gangue result in a desirable ore when it is so graded that the P presents no problem in steel production, as in the basic Bessemer process.

As shown by the lower curves of Fig. 1, the production of concentrates has ranged between 1 million and 1½ million tons since 1936. Practically all concentrates now are sintered in batch type equipment of the Greenewalt type.

The goal of Swedish sintering practice is to produce a strong, porous product consisting largely of hematite. In the United States, porosity and strength have been recognized as criteria of sinter

T. L. JOSEPH is Professor of Metallurgy at the University of Minnesota, Minneapolis. This paper was presented at the Blast Furnace, Coke Oven, and Raw Materials Conference, Cleveland, Apr. 2 to 4, 1951.

Fig. 1—Swedish production and exports of iron ore, concentrates, and sinter. (Data from Jernkontoret Annaler, 1950, Vol. 134, No. 2.)

quality; but until recently little attention has been given to the degree of oxidation. Tigerschiold[1] pointed out that it has been recognized in Sweden that a preliminary oxidizing roast of dense magnetite lowered consumption of charcoal in blast furnaces. This fuel reduction was attributed to the higher reducibility and more indirect reduction. The roasting was carried out so as to convert most of the Fe_3O_4 to Fe_2O_3 without forming silicates. As part of the effort to save fuel, production of oxidized sinter appeared to be a logical objective and was achieved after several years of development.

As a result of a study of the sintering process and essential features of practice that contribute to producing good *black burned* sinter, Hessle[2] concluded that temperature control was of basic importance. The term *black burned* sinter refers to a sinter free of glazed surfaces that are characteristic of hard burned sinter. *Black burned* sinter also is free from large holes and has a uniform cellular structure, indicative of fritting without vitrifaction.

To achieve these characteristics a temperature necessary to frit the particles together must be attained but not exceeded, else glazed or vitrified surfaces are produced. Hessle emphasized that the period of time at and immediately below this critical temperature must be short. Uniform mixing of the charge, loose and uniform charging, simultaneous and uniform ignition, fine crushing of fuel, and a plentiful air supply are details of practice that must be adhered to rigorously to insure a close control of temperature throughout the bed. The sides of the pan are sloping to minimize channeling along the edges of the bed. A loosely packed charge is preferred because it yields a more compact sinter. Certain tests are necessary to follow conditions essential for close control. To control mixing, the moisture content, quantity of fuel and screen analysis must be checked periodically. To show the degree of control exercised in the Hofors Steel Works, moisture in the mix is run six times per hr. Waste gas temperature, suction, and the temperature gradient in the bed are means of following conditions in the charge. Weight of sinter per pan, screen analysis, sulphur content, and the degree of oxidation are criteria of sinter quality, an essential forerunner of quality steel.

Care is taken in proportioning and mixing of raw materials in various Swedish sintering plants. Batch type sintering and the use of ore fines or concentrates of fairly uniform screen size are factors that help produce sinter of high quality. The general opinion is that Swedish sinter is considerably weaker than that produced in United States. Hamilton[3] and Ameen reported that crushing and tumbler tests show that Swedish sinter broke down more than sinter of the type made in this country. Regardless of strength, an important consideration is that Swedish sinter is so handled after it is produced that it normally enters the blast furnace in pieces 2 to 3 in. diam with relatively small amounts of small sizes being present.

Current methods of handling sinter in this country after it is produced need improvement. The need of making sinter strong enough to resist breakage when subjected to present methods of handling is open to question. Saussaman[4] described a system of handling sinter and has given the attendant blast furnace performance that speaks well

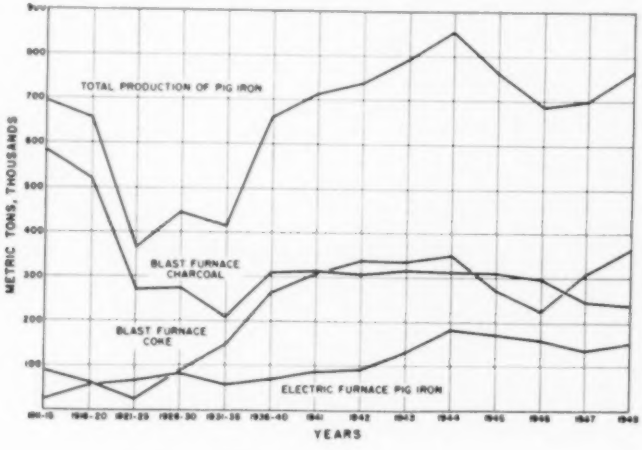

Fig. 2—Swedish production of pig iron.

for careful treatment to avoid size degradation. He stated: "The sinter (Fontana) is very porous and comparatively soft and consequently will disintegrate into excessive amounts of fines if handled roughly or quenched with large quantities of water." One pertinent feature of the Fontana sinter is that it contains about 7.53 pct SiO_2 plus Al_2O_3 and 8.17 pct CaO plus silica. This self-fluxing character and the fact that it contains more than a normal percentage of total iron as hematite are common features of Fontana and Swedish sinter. The production of a highly oxidized, self-fluxing sinter is worthy of careful consideration, even though considerable modification of present sintering practice and a more careful handling of the sinter may be necessary. Sinter that must withstand shipping should be stronger than a product made at the furnaces. However, sintering or agglomerating plants should not be built at long distances from the furnaces except after careful consideration of the advantages of a readily reducible product, which can be carefully handled in transit to the blast furnace.

Total production of pig iron in Sweden has ranged from about 700,000 to 850,000 tons except from 1920 to 1936. As shown in Fig. 2, most pig iron was produced in charcoal blast furnaces until about 1931 when the production from coke blast furnaces began to rise sharply. Since 1936 production of charcoal and coke pig iron have been about equal, each averaging about 300,000 tons per year. The ascendency of coke blast furnace pig over charcoal pig, evidenced since 1947, will become much more pronounced when an 800 ton coke blast furnace under erection in the Government-owned plant at Lulea is operating. This is the only blast furnace in Sweden comparable in size to those in United States. Electric furnace pig iron has exceeded 100,000 metric tons since 1942 and production records since then indicate this method of producing pig iron is well established. A mixture of about equal amounts of charcoal and coke breeze makes a good fuel for the electric furnace. Electric furnaces are not as sensitive to variations in the physical character of raw materials as are blast furnaces. Low sulphur iron of high quality can be produced from poor raw materials. The top gas is

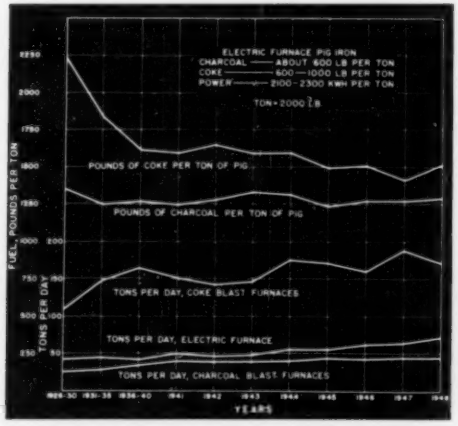
ELECTRIC FURNACE PIG IRON
CHARCOAL —— ABOUT 600 LB PER TON
COKE ——— 600—1000 LB PER TON
POWER ——— 2100-2300 KWH PER TON
TON = 2000 LB
POUNDS OF COKE PER TON OF PIG
POUNDS OF CHARCOAL PER TON OF PIG
TONS PER DAY, COKE BLAST FURNACES
TONS PER DAY, ELECTRIC FURNACE
TONS PER DAY, CHARCOAL BLAST FURNACES
FUEL, POUNDS PER TON
TONS PER DAY
YEARS

Fig. 3—Daily production and fuel consumption of Swedish pig iron furnaces.

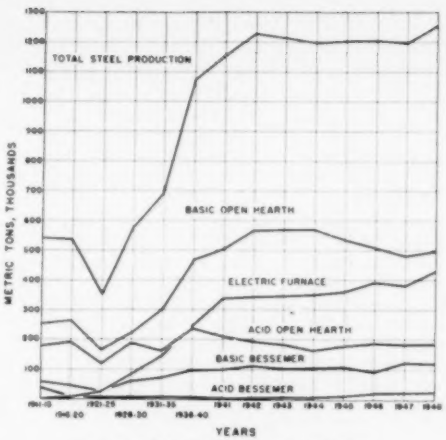

Fig. 4—Swedish steel production by processes.

largely CO and H_2 with a calorific value of about 290 Btu per cu ft. Daily capacity, however, is low and repair and labor costs are rather high. Overall economy depends largely upon favorable power costs.

Concentration of iron ore to reduce slag volume and production of high quality sinter has led to a reduction in coke consumption in Swedish blast furnaces. Average coke rates have fallen from about 2250 lb in 1926 to 1930 to a low of 1412 lb per net ton in 1947, as shown in Fig. 3. This indicates efficient operation of small units, regardless of high heat losses in the crucible. Although Fig. 3 indicates the consumption of charcoal has remained steady, it actually has decreased gradually since 1936 because of a change made that year in the method of measuring charcoal. The use of large amounts of sinter of improved quality has reduced the consumption of fixed carbon more than 10 pct because the quality of the charcoal has deteriorated.

Production of coke blast furnaces has increased from about 150 to 175 tons per day. Electric furnaces are next in productivity with an increase from about 40 tons per day in 1943 to about 70 tons per day in 1948. The output of charcoal pig iron furnaces has remained steady at about 40 tons per day. These daily tonnages appear small to American operators, but are, however, consistent with the conditions in Sweden and the emphasis on quality steel production.

Production of Swedish steel rose steadily from 350,000 tons in 1921 to 1925, to 1,228,000 metric tons in 1942, as shown in Fig. 4. It will be noted that production was rather steady from 1942 to 1948. In 1949 and 1950, the total annual production of steel was 1,370,000 and 1,438,000 metric tons, respectively. Since 1936, about 500,000 tons of basic open hearth steel has been produced annually. Electric furnace steel had a rapid growth from about 25,000 tons per year in 1921 to 1925, to a peak of 431,000 tons in 1948. For the years 1946, 1947 and 1948, production of open hearth steel averaged 495,000 tons per year compared with 402,000 tons of electric furnace steel. Acid open hearth ranks next to electric furnace steel from a tonnage standpoint. Annual production from this process ranged

from 120,000 tons in 1921 to 1925, to 236,600 tons in 1936 to 1940. A comparison of the percentage distribution of steel production by method for the United States and for Sweden in 1948 follows:

	United States	Sweden
Electric furnace, pct	5.7	34.4
Acid open hearth, pct	0.7	14.6
Basic open hearth, pct	88.0	39.2
Bessemer, pct	4.6(acid)	11.8(acid + basic)
Total	100.0	100.0

Half of the steel produced in Sweden is made by quality processes, which must be kept in mind in all considerations from the treatment of raw materials on through to the finished product. Melting stock for the acid open hearth and the electric furnace is important.

In a recent paper, Farley and McCurdy[5] reported that the electric furnace process, with greatly expanded capacity since World War II, is in a critical position. Its capabilities are limited by the character of the scrap, which governs good charging, fast melting, reliable chemical control, melt down, and freedom from injurious contamination. They further pointed out that contamination may make the melt worthless for the planned grade, may result in the purchase of worthless materials at the price of good scrap, may be destructive to the furnaces, and may present serious safety hazards. Elements such as copper, nickel, chromium, and molybdenum that can not be removed from the bath by oxidation present a problem in the close control of composition. Melting stock for the acid open hearth and the electric furnace has received attention in Sweden because quality steel is such a large proportion of total production. As pointed out by Tigerschiold,[6] Sweden has been producing sponge iron commercially since 1911 by the Hoganas process. In this process, refractory crucibles filled with alternate layers of solid fuel, crushed limestone, and ore are heated in kilns until the ore layer is reduced to metal that is sintered into a cake. It is natural that the possibilities of using sponge iron as a source of virgin metal for the acid open hearth as well as the electric furnace have been considered seriously in Sweden for the past 20 years because of the shortage and high cost of charcoal pig iron and of high-grade scrap. Moreover, the production of sponge iron requires relatively small amounts of fuel, which need not meet all of the requirements of blast furnace fuel.

The Wiberg process described by Kalling and Stalhed[7] has been used at Soderfors, a tool steel plant, for a number of years. This plant operates two 6-ton induction furnaces, a 5-ton and a 10-ton arc furnace. The charge for the arc furnaces generally consists of 70 pct sponge iron and 30 pct home scrap. According to Tigerschiold[6] the cost of sponge iron produced at the rate of 20,000 tons a year by the Wiberg method will range from $26.72 to $35.07 per ton.

The Sandviken Steel Co., which has used sponge iron in acid open hearth charges for many years, has been operating a pelletizing furnace for the agglomeration of fine magnetite concentrates. Pellets, approximately 1 in. diam and made in a shaft furnace of the type developed at the Mines Experiment Station of the University of Minnesota,[8] have been used successfully in trial runs with the 30-ton Wiberg sponge iron furnace at Soderfors. Under the guidance of Jernkontoret, several companies are participating in a development involving: 1—The production of rich concentrates, 68 pct Fe or higher; 2—The agglomeration of these concentrates by the pelletizing process; and 3—The reduction of these pellets in a Wiberg shaft furnace.

A porous, light burned sinter is used in the Wiberg sponge iron furnace at Soderfors, but encouraging results have been obtained with pellets. Interest in the production of concentrates of very high iron content seems to be increasing.

At Malmberget, the Kiirunavaara-Loussavaara Co. is producing a concentrate containing about 71.5 pct iron, about 0.6 pct SiO_2 and 0.010 pct P max. Concentrates containing about 71.7 pct iron and 0.15 to 0.20 pct SiO_2 have been produced for use in the Hoganas sponge iron process. To produce such high grade concentrates, the ore is ground to fine sizes to liberate the silica. The pelletizing process fits into the overall picture because it is a means of agglomerating very fine concentrates that would be difficult to sinter. Large pelletizing plants and larger sponge iron plants are being built in Sweden. These plants will provide additional information on costs and operating practices.

The incentive to produce high quality melting stock in Sweden is great. Solutions probably will be found to all minor problems and in the end sponge iron may gradually replace charcoal pig iron in the production of Swedish quality steel.

Production of sponge iron has not been a commercial success in the United States. In view of the need for better sources of electric furnace scrap, it appears that further work should be carried out to test the feasibility of making a high grade concentrate from New York magnetites. These could be reduced in a shaft furnace of the Wiberg type after pelletizing. The Wiberg process operates smoothly and is fully mechanized, requiring only two men per shift for operation. The use of a sulphur-free mixture of three parts of CO to one part of H_2 for reduction is a novel and important feature of the process. This permits reduction without an overall absorption or evolution of heat, and close control of temperature which is important to avoid sticking and mechanical difficulties in a shaft furnace is maintained.

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CONTROL OF

SULPHUR IN STEELMAKING

by G. Derge and S. Marshall

Because of the trend toward less satisfactory raw materials and the increasing importance of sulphur control, a Sulphur Symposium was held at the AIME Annual Meeting. This is a report of the technical highlights of that meeting.

THE American iron and steel industry has recognized a sharp trend toward less satisfactory raw materials, which will necessitate increased attention to all phases of production related to sulphur control. This has led to a large amount of laboratory and mill research on the metallurgical reactions and processes involved in desulphurization. In order to focus attention on this research and coordinate the information with operating conditions, the Physical Chemistry of Steelmaking Committee of the Iron and Steel Div., American Institute of Mining and Metallurgical Engineers, organized a two-day Sulphur Symposium for the annual February meeting. The Symposium Committee consisted of C. R. Taylor, chairman, and L. S. Darken, N. J. Grant, and C. Hogberg.

The program opened with a discussion of the scientific background of the problem. The morning session was under the chairmanship of W. O. Philbrook, Carnegie Institute of Technology, and John Pollock, Jones and Laughlin Steel Corp. The first two papers dealt with oxide-gas equilibria. It is a general belief that the effective agent in most desulphurizing systems is lime. The paper by Terkel Rosenqvist, University of Chicago, approached the problem so as to provide a basis for thermodynamic calculations of the desulphurizing power of lime containing slags by obtaining data on the gas-solid reaction:

$$CaS_{(s)} + H_2O_{(g)} + H_{2(g)} \rightleftharpoons CaO_{(s)} + H_2S_{(g)} + H_{2(g)}$$

The reaction was studied in the temperature range 750° to 1425°C by passing a steam-hydrogen mixture of controlled composition over a composite porous plug of crystalline CaS and CaO and analyzing the effluent gas for H_2S. The data show a free energy change for the reaction of

$$\Delta F^\circ = -RT \ln \frac{H_2S}{H_2O} = 15{,}650 - 0.87\ T \text{ cal.}$$

The crystalline form of lime in this system may be regarded as the standard state of this material and suitable combination with other data allows the evaluation of the desulphurizing action of lime in systems involving other slag constituents. Applications to blast furnace slags were suggested in terms of ionic theory.

In another series of experiments, the steam-hydrogen mixture was bubbled through molten copper in contact with solid CaO and CaS and the sulphur content of the copper. For the reaction

$$S_{(\text{in Cu})} + CaO_{(s)} + H_{2(g)} = CaS_{(s)} + H_2O_{(g)}$$

the equilibrium ratio

$$\frac{H_2O}{H_2 \times \text{Pct } S_{(\text{in Cu})}}$$

was 0.55 for a 1 pct solution.

The more complicated situation involved in slag-gas systems was reported by L. S. Darken and B. M.

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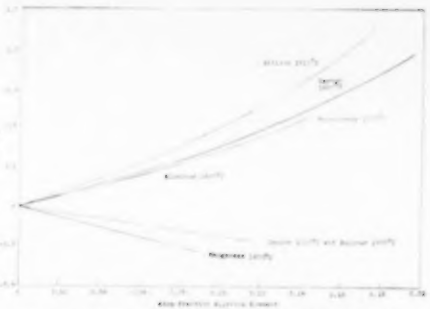

Fig. 1—Activity coefficients for sulphur for alloys of iron with manganese, phosphorus, aluminum, carbon, silicon, and copper.

Shields of United States Steel Research Laboratory who studied CaO-Fe_2O_3 slags equilibrated with various controlled gas atmospheres (SO_2-O_2, SO_2-air, SO_2-CO_2 or SO_2-CO_2-CO) in the temperature range 1300° to 1620°C. A typical basic open hearth slag also was included. They found that with about 8 pct SO_2 in the gas, the sulphur content of a 50 pct CaO slag was about 1 pct and that this decreased to an immeasurably small amount when the CaO content was reduced to 8 pct at high temperature. To explain the observed influence of temperature, pressure, and slag composition, it was necessary to assume substantial amounts of pyrosulphate (CaS_2O_7 or $S_2O_7^=$) present in the slag, the relative amount of this compound being negligible at 1600° and high basicity, but becoming significant at the other end of the range studied. The dependence upon oxygen pressure is such that at 1600°, the sulphide form predominates when the gas contains more than 6 pct CO. The Fe_2O_3 content of open hearth slags is low compared to that observed in these experiments, and this was interpreted to mean that the iron bath maintains the slag at a low oxygen potential corresponding to the range of stability of sulphide.

Sulphur Activity in Liquid Metal

Two correlated papers dealt with the influence of alloying elements on the sulphur activity in liquid iron and steel. Charles W. Sherman and John Chipman of Massachusetts Institute of Technology reviewed existing information on the activity of sulphur in iron and steel, including data from the following paper by J. P. Morris, Pittsburgh Station, U. S. Bureau of Mines. New experimental data were presented for alloys of iron with manganese, phosphorus or aluminum, and activity coefficients for sulphur were derived for these alloys as well as those of iron with carbon, silicon, and copper, as shown in Fig. 1. The logarithms of these coefficients are additive in a multicomponent system and when applied to pig iron the analysis shows that sulphur has about five times the escaping tendency that it would have in pure iron at the same weight per cent concentration.

Morris gave a detailed description of the experimental procedures used at the Bureau to obtain data on the effect of C, Mn, and Si and presented the data in Fig. 2 on the solubility of sulphur in carbon saturated iron melts as a function of manganese content in equilibrium with an MnS-FeS matte. The curves show that although manganese limits the sulphur solubility, very appreciably at low temperatures, the effect is not enough to be of value under operating conditions.

The general agreement between these papers on both data and interpretation gave every indication that this particular phase of the problem is now well understood. Another feature of the morning session was the trend toward consideration of slag reactions in ionic terms. However, discussion on this topic brought out the fact that ionic interpretation is still in its development stage.

Slag-Metal Reactions

The afternoon program provided the transition to furnace problems, dealing with slag-metal reactions under laboratory controlled conditions. The co-chairmen were Charles Taylor of Armco Steel Corp., and D. C. Hilty of Union Carbide and Carbon Research Laboratories. All papers dealt with slightly oxidizing or reducing conditions and may be considered as pertinent to blast furnace or electric furnace practice rather than open hearth practice.

The influence of Mn and MnO on the desulphurization process in the blast furnace was the principal objective of the studies reported by N. J. Grant, Bo Kalling, and J. Chipman of the Massachusetts Institute of Technology. They used synthetic slags simulating blast furnace compositions, but selected to show the influence of basicity and the relative effectiveness of CaO and MgO on the reaction. Compositions and results are shown in Table I. These slags were used to desulphurize metal with an initial composition of 1.65 pct sulphur in a graphite crucible designed to provide vigorous mechanical stirring by a rotating screw as shown in Fig. 3. The time required to reach sulphur equilibrium for each slag is shown in the last column of Table I, confirming the recognized effectiveness of high basicity. The influence of MnO and Mn was observed by making additions of these materials during the heat, and in all cases they caused a sul-

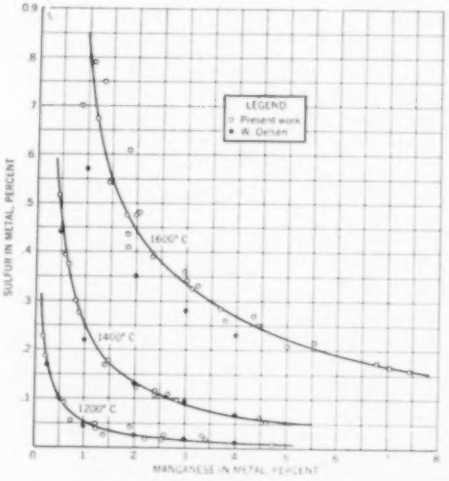

Fig. 2—Effect of manganese on the sulphur content of carbon-saturated melts of iron in equilibrium with MnS-FeS slag.

Table I. Synthetic Slag Compositions

Slag No.	Starting Slag Compositions, Weight, Pct CaO	MgO	SiO_2	Al_2O_3	Approx. Hr for S Equilibrium
a	50	2	33	15	6
b	50	10	25	15	1
c	40	2	43	15	12
d	40	10	35	15	10 to 12

phur reversion to the metal that was attributed to the reoxidation of the slag by reduction of MnO. It also was noted that manganese recovery was best with the basic slag. MgO did not appear to be as good a desulphurizer as CaO. All observations pointed to the importance of slag oxidation in limiting the process.

The same experimental procedure and slags b and d of Table I were used by N. J. Grant, O. Troili, and J. Chipman to observe the effect of silica reduction on desulphurization. In these experiments, 1 to 4 pct Si was added to the iron at the start of the run. It was shown that with 3.92 pct Si in the initial bath, additional Si was reduced from slag d during the run. This reduction was so slow that an estimated 10 hr would be required to approach equilibrium. The time required to attain sulphur equilibrium was least with the high silicon runs. This indicated that oxygen released by rapid SiO_2 reduction in low silicon runs retarded the desulphurization reaction. For the more basic slag b, it appeared that equilibrium was approached after 9 hr with about 1.4 pct Si in the metal.

The degree to which iron in an operating blast furnace achieves equilibrium with its own slag was examined by E. W. Filer and L. S. Darken of United States Steel Research Laboratory by remelting samples of blast furnace iron and slag (taken simultaneously) in graphite crucibles and a CO atmosphere. Experiments were extended from 1 to

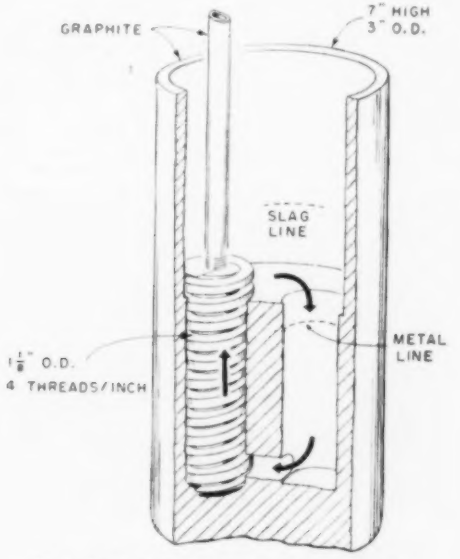

Fig. 3—Sketch of modified graphite stirrer and crucible.

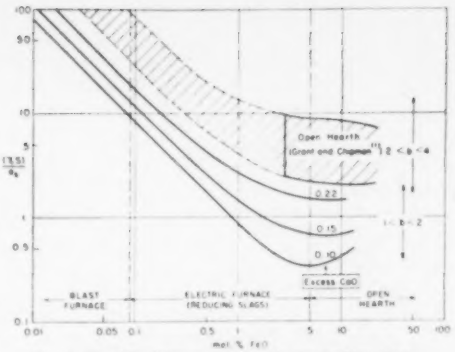

Fig. 4—Desulphurizing power of basic steelmaking slags. (Neutralization of the acids on 1:1 basis.)

66 hr over a temperature range from 1400° to 1600°C. The longer 1600° runs showed appreciable losses of silicon, manganese, and magnesium by volatilization but relatively little loss of calcium, sulphur, aluminum, and iron. Comparison of the compositions in Table II shows that the original metal and slag are not in equilibrium except possibly with respect to silicon; the sulphur distribu-

Table II. Composition of Metal in Equilibrium with Blast Furnace Slag

Pct	Original	1400°C	1500°C	1600°C
S	0.028	0.017	0.010	0.008
Si*	1.01	0.5	1.4	(4)
Mn*	2.04	2.1	2.4	2.6
(Si/S	94.	89.	134.	205.

* Corrected for evaporation.

tion ratio and manganese recovery are more favorable at equilibrium than in the blast furnace. This equilibrium was reached within 1 hr for sulphur, but required about 10 hr for manganese.

In separate experiments, sulphide additions were made, and it was found that calcium sulphide crystals appeared as a separate phase when the slag contained more than 4.5 pct.

The observed differences between desulphurization in open hearth and blast furnaces never have been completely explained on theoretical grounds. The work reported by R. Rocca, N. J. Grant, and J. Chipman approached the problem by observing sulphur distribution between iron and slag over a range of low iron oxide concentrations. These conditions were comparable to those encountered during the reducing period in the electric furnace. The iron oxide in the slags ranged from 0.08 to 15 pct. Deoxidation was controlled by additions of silicon metal. Desulphurization was measured by the ratio of:

$$\frac{(\text{Pct S})}{a_s} = \frac{\text{Pct in the slag}}{\text{activity in the metal}}.$$

The results show that there are two important factors: 1—Increasing concentration of excess lime favors desulphurization. 2—Decreasing concentration of iron oxide in the slag favors desulphurization.

The latter factor becomes controlling when (FeO) is lower than 2 mol pct. The results are summarized and correlated with other operating conditions in Fig. 4. Under the reducing conditions of the blast

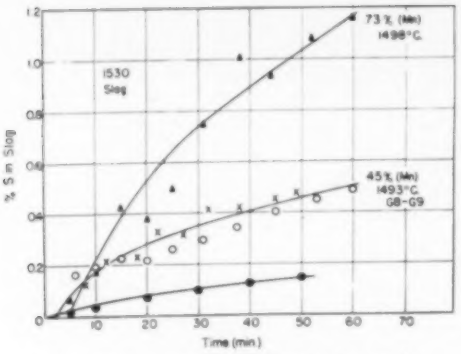

Fig. 5—Effect of manganese additions to iron on the rate of desulphurization.

furnace, most of the sulphur is held in the slag as CaS, while in the more oxidizing slags of the electric furnace and open hearth it may be present as both CaS and FeS.

The kinetic study of sulphur transfer presented by G. Derge, W. O. Philbrook, and K. M. Goldman of Carnegie Institute of Technology differed from the earlier papers on the program, which included observations on reaction mechanisms resulting from equilibrium studies, in that it had the determination of the influence of Mn and Si on reaction rate and mechanism as its primary objective. This completed the picture by extending observations to the initial stages of desulphurization, whereas the other papers dealt mostly with the end of the process as equilibrium was approached. Previous work had indicated three principal stages in the process in a carbon saturated system but without intentional alloy additions:

(1) $FeS_{(in\ m)} \rightleftharpoons FeS_{(slag)}$

(2) $FeS_{(slag)} + CaO_{(slag)} \rightleftharpoons CaS_{(slag)} + FeO_{(slag)}$

(3) $FeO_{(slag)} + C_{(in\ metal)} \rightleftharpoons Fe + CO_{(gas)}$

Slags were of the CaO-Al_2O_3-SiO_2 type covering the normal range of interest for blast furnace applications.

Initial alloy additions to the iron of Si or Mn increased the rate of desulphurization markedly as shown in Fig. 5 and 6. However, auxilliary evidence showed that the mechanism is different for the two elements. Manganese adds its influence to that of iron as a sulphur carrier across the slag-metal interface in reaction (1), while silicon seems to accelerate the otherwise slow reaction (3), probably by substituting for C and reducing FeO in the slag without the necessity for bubble formation. Data were shown to indicate similar functioning of Mn in an operating blast furnace.

Considered as a group, the papers indicated desulphurization does not necessarily reach equilibrium in many commercial processes, and that both equilibrium and the rate at which it is approached are sensitive to the variations of slag composition and metal analysis.

External Desulphurization of Pig Iron

The more practical aspects of the sulphur problem were considered on the second day of the Symposium. Co-chairmen for the morning session were T. L. Joseph, University of Minnesota, and W. E. Marshall, Armco Steel Corp.

S. D. Baumer and P. M. Hulme, Air Reduction Co., New York, presented the results of experiments designed to desulphurize hot metal with calcium carbide. They pointed out the difficulties encountered in reacting a solid reagent with liquid iron, and showed the method employed to promote the dispersion of calcium carbide in a liquid bath. About 1 lb of sulphur could be removed for an expenditure of 10 lb of calcium carbide—in treating small batches, up to 400 lb—and the resulting slag contained about 13 pct sulphur. No reversion of sulphur was noted, even after prolonged holding time, unless fluxing agents were employed to render the slag fluid. Pilot plant tests, in which iron flowing from a cupola at 6 tons per hr was treated continuously with carbide, confirmed laboratory observations with regard to the efficiency of calcium carbide in removing sulphur.

A method of desulphurizing hot metal by burnt lime and coke was described in a paper by Bo Kalling, Christer Danielsson and Ottar Dragge, Stora Kopperbergs Bergslags AB, Domnarvet, Sweden. A rotating furnace is used to promote intimate contact between solid lime and liquid iron. The furnace is closed during the reaction to prevent access of oxidizing gases, and the sulphur content of the iron can be reduced to very low values in a short time. The process will not operate satisfactorily unless the lime remains in powder form throughout the operation. Consequently, the temperature must not be too high. Above 1400°C the lime will "ball up" or stick to the furnace walls, thus inhibiting the reaction.

The experimental work was carried out at Domnarvet in a furnace of 2 to 3 tons capacity with a rotation speed of 40 rpm. Sulphur contents, of the order of 0.005 pct, were attained without difficulty. Also, it was possible to reduce sulphur to low values in one operation even though the sulphur content of the iron from the blast furnace was abnormally high. In one experiment the sulphur content was reduced from 0.350 pct to 0.003 pct in a single operation by treating the hot metal with 3.8 pct of burnt lime and coke breeze. In another experiment the sulphur content of iron containing 0.100 pct sulphur was reduced to 0.010 pct in 5 min by the use of 1.5 to 2.0 pct of burnt lime and coke breeze.

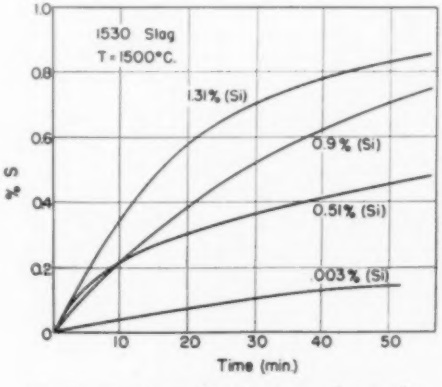

Fig. 6—Effect of silicon additions to iron on the rate of desulphurization.

Ordinarily the temperature of the iron decreases by about 50°C during the desulphurizing operation, even when the rotating furnace is preheated to 1100°C. However, if the furnace is carefully insulated and operations are not too intermittent, it is possible and advantageous to omit preheating. Since no molten slag forms, attack on the furnace lining is very slight.

The operation of the Kalling-Domnarvet desulphurizing process at the Surahammars Bruks AB, Surahammar, Sweden, was described in a paper by Sven Fornander. Hot metal from the blast furnace was tapped into a 15-ton ladle and transferred to the rotating furnace, Fig. 7. An addition consisting of finely ground burnt lime amounting to 2 pct of the weight of the hot metal, and 0.5 pct of coke breeze is made to the furnace. The furnace is then sealed from the atmosphere and set in rotary motion at a rate of 34 rpm. The sulphur is rapidly absorbed by the lime and the time of treatment is normally 30 min. When the process is completed the furnace is uncovered and the iron poured into pig molds. Fig. 8 gives an example of the change in hot metal composition as a result of the desulphurizing treatment. The sulphur content decreases rapidly during the first 10 min from about 0.090 pct to about 0.020 pct. During the following 20 min the sulphur content decreases slowly to about 0.005 pct; carbon, manganese, silicon, and phosphorus concentrations change only slightly. The chemical reaction taking place during the process is believed to be

$$2FeS\ (\text{in liq. Fe}) + Si\ (\text{in liq. Fe}) + 2CaO\ (\text{solid}) = 2CaS\ (\text{solid}) + SiO_2\ (\text{solid}) + 2Fe\ (\text{liq.})$$

The process is unique in the metallurgy of iron and steel in that a solid phase reacts actively with a liquid metal. No liquid slag is formed in the process; the *lime*—reaction products—remains in the form of a fine powder.

The process is being applied continuously and gives uniform results provided certain precautions are observed. The lime should be as pure as possible especially with respect to silica, carbon dioxide, and water. It can be said that if the silica content of the lime exceeds 5 pct the sulphur content of the treated iron will exceed 0.010 pct. If good desulphurization is to be obtained, it is important that the furnace not be exposed to oxidizing conditions either during the treatment of the metal or during the time elapsing between treatments.

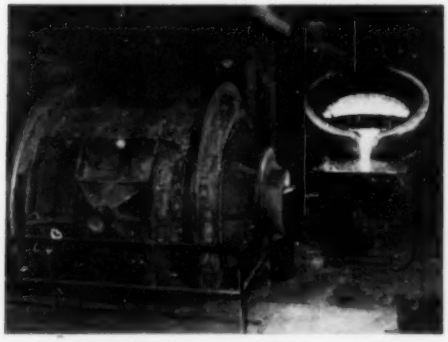

Fig. 7—Rotating furnace used in the Kalling-Domnarvet desulphurizing process.

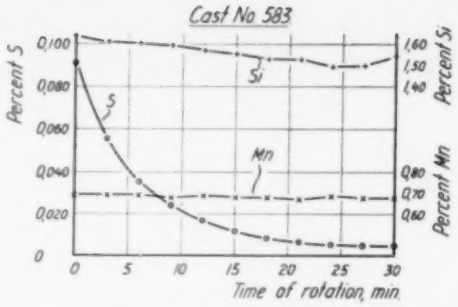

Fig. 8—Change in hot metal composition during the desulphurization treatment.

Desulphurization in the Open Hearth

The afternoon session, with co-chairmen H. L. Tear, Jones & Laughlin Steel Corp., and Shadburn Marshall, United States Steel Co., started with a paper by F. L. Robertson and E. H. Bacon, John Summers & Sons, Ltd., entitled "*The Making of Low Sulphur Steel from High Sulphur Raw Materials and High Sulphur Fuel by the Cold Metal Process.*" In producing low carbon deep drawing steels no difficulty was encountered in meeting specifications of 0.025, 0.030 and 0.035 pct sulphur until some of the furnaces were converted from producer gas fuel to oil containing 2.5 pct sulphur. To study the problem a detailed survey was made on an 84-ton furnace over an extended period of time. The time of heat was divided into two periods: *(1) Start Charge to Clear Melted or Junction;* and *(2) Junction to Tapping.* Junction was defined as the time at which the steel temperature, as measured by an immersion pyrometer, reached a figure corresponding to the carbon content on an arbitrary carbon-temperature curve.

The important points brought out in the investigation were:

(1) The partition of sulphur between slag and metal, $\frac{(S)}{[S]}$, at *junction* varied greatly.

(2) The ratio $\frac{(S)}{[S]}$ at *tap* varied considerably, but most values were above 6.

(3) The pickup of sulphur by the liquid system from the furnace atmosphere varied widely, but on the average the increase from start charge to *junction* was 30 lb; from *junction* to *tapping*, nil.

The results further showed that no proper understanding of the behavior of sulphur in the liquid phases could be reached without taking into account the weight of slag, the weight of steel, the weight of sulphur in each, as well as the percentages of sulphur in slag and metal. In working out a method for calculation of the feed lime required it was not regarded as feasible to predict $\frac{(S)}{[S]}$ at tap by any of the usual basicity measurements. As a basis for a process the ratio was arbitrarily assigned a value of 6. Charts were prepared showing the relations between pounds of sulphur in steel and

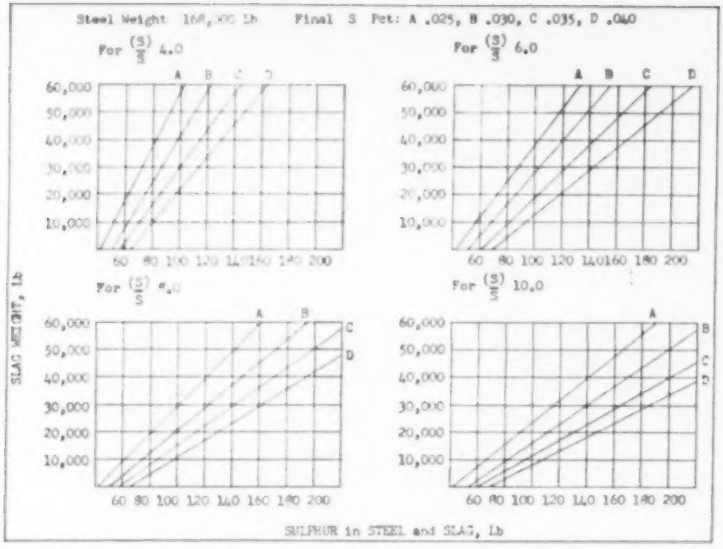
Steel Weight 168,000 Lb Final S Pct: A .025, B .030, C .035, D .040
For (S)/[S] 4.0
For (S)/[S] 6.0
For (S)/[S] 8.0
For (S)/[S] 10.0
SLAG WEIGHT, Lb
SULPHUR in STEEL and SLAG, Lb

Fig. 9 — Relations between sulphur in steel and slag, (S)/[S], specified sulphur content, and slag weight for 84-ton heats.

slag, $\frac{(S)}{[S]}$, specified sulphur content, and slag weight for 84-ton heats, Fig. 9. Slag weight was calculated using lime as basis.

The process evolved for producing steel of a specified sulphur content is:

(1) Calculate the charge to give a carbon content at *junction* of 0.3 to 0.5 pct.
(2) Calculate the weight of lime to give a "V value" of 4 at *junction*.
(3) Weigh the charge to an accuracy of ± ½ ton.
(4) Analyze metal and slag at *junction*, calculate the total weight of sulphur assuming the slag weight to be twice that of the lime charged.
(5) Calculate the required lime addition from previously prepared charts.

The process has worked out and has been in operation for over 2 years on all furnaces. The desired sulphur content in the steel can be attained by the process but usually at the expense of large slag volumes.

D. E. Babcock, Republic Steel Corp., in his paper "*The Application of Physico-Chemical Principles to Open Hearth Desulphurization Problems*," pointed out some of the complications involved when the metallurgist attempts to apply the results of research workers in the analysis and solution of problems of day to day open hearth operations.

Taking the data of Grant and Chipman for the distribution of sulphur between slag and metal, he outlined the enormous number of mathematical operations that must be made to express these data in a form useful for computation of the results obtainable in an open hearth furnace with molten iron under a slag system which can be changed in composition as desired to meet a specific problem. It was pointed out that errors in such complex calculations can be avoided by tabularizing the computation, and an example of such a procedure was given.

T. E. Brower and B. M. Larsen, United States Steel Co., presented a survey of the sulphur problem in various operations in the steel plant. In the smelting phase, ore to hot metal, nearly all the sulphur that enters the system comes from the coke. Because of the rising sulphur content of available coking coals, it appears inevitable that a gradual rise in sulphur input to the blast furnace will occur. By increasing the MgO content of the slag to 6 to 8 pct, a better elimination of sulphur seems possible without loss of production. Most other proposed methods for carrying more sulphur in the blast furnace involve a small loss in iron production rate. Operating data for seven periods in various furnaces were given showing coke sulphur varying from 0.80 to 1.80 pct with average sulphur in the iron held to the range 0.030 to 0.042 pct, indicating that the blast furnace can handle some extra sulphur without serious handicap.

Various techniques for desulphurizing iron with alkalis or other basic materials outside the furnace have suffered from imperfect control and variable efficiency. Sulphur elimination by precipitation of MnS during transit of hot metal to a mixer requires too much cooling of the metal unless the manganese content is very high, of the order of 3 pct.

In the open hearth, the dominating factor is the limited amount of sulphur that can be eliminated by the slag, so all sources of sulphur input must be carefully watched. Open hearth fuel normally carries more sulphur into the system than all other materials, but with fuel of moderate sulphur content, not more than 1 to 2 pct of this sulphur is absorbed by the slag-metal system. With high sulphur fuels such as oil with 2.5 to 3.5 pct sulphur or coke-oven gas with 500 to 600 grains per cu ft, this sulphur pickup may rise to 4 to 7 pct and the steel may retain an extra 3 to 20 points of sulphur.

Acknowledgment

The writers of this article wish to thank the authors of the various papers for providing such excellent abstracts of their work that this contribution was only one of condensation and coordination.

Separation of Copper from Zinc by Ion Exchange

by Ernest J. Breton, Jr. and A. W. Schlechten

Experiments on the separation of copper and zinc ions by selective action of ion exchange resins showed the carboxylic type to be more effective than the sulphonic resins. The latter demonstrated a greater capacity over a wider pH range. Data show the effectiveness of resins as a means of concentration.

IN recent years the restrictions of stream pollution laws and the high price of metals have created an interest in ion exchange as a means for metal recovery. Some applications have proved successful. In Germany during World War II, 17 tons of copper per day were recovered from rayon mill wastes by means of ion exchange resins;[1] and for some time in this country a large ion exchange unit has been in operation for the recovery of copper from rayon waste water. The possibilities of applying ion exchange to the recovery of metals occurring in plating rinse water is particularly promising.

In most of these applications only the metal being recovered occurs in the waste. The ion exchange resins act merely as a means of concentrating the metals to a point where they can be recirculated. It would be highly desirable to use ion exchange as a means of not only concentrating but also of separating metals. With the exception of the impressive separations accomplished in connection with the atomic energy program, very little has been done on metal separations.[2] Therefore, an investigation was undertaken at the Missouri School of Mines and Metallurgy to determine if either of the two main types of ion exchange resins could be used to separate metal ions in solution. The selective removal of copper ions from a mixture of copper and zinc on carboxylic and sulphonic-type resins was investigated as a function of flow rate, pH, copper-zinc ratio, and concentration. It was shown that zinc can be separated from copper and that very large ratios of concentration can be obtained using ion exchange resins. Since ion exchange is relatively new to the field of metallurgy, a brief review of the subject will be included.

Theory of Ion Exchange

A comprehensive theory for ion exchange has not been developed as yet, but the mechanisms are analogous to metathetical reactions:

$$R\,Na + Cu^{++} \leftrightarrows R(SO_3)_2\,Cu + 2Na^{+}$$

R is the designation for the ion exchange resin. If a copper solution is passed over a resin bed in the sodium form, two ions of sodium will be released for every ion of copper removed. For the most part this reaction follows the laws of mass action and of electrical neutrality. Consequently, if an excess of sodium ions is passed over a bed containing copper, the reactions will be reversed, and the resin will be regenerated to its original form.

A few empirical rules governing the exchange reaction have been set forth: 1—In general ions with a high valence will replace ions with a lower valence. 2—Ions having higher activity coefficients have a higher replacement potential. 3—In a series of monovalent ions, those with the smallest radii of hydration will tend to replace those having larger radii of hydration. 4—Where ions are similar in most respects, those with the higher atomic weight sometimes will take precedence. This last rule is not as definite as some of the others. These rules apply to rather dilute solutions at moderate temperatures and assume all ions to be present in about equal concentrations. Higher concentrations and temperatures may in some cases reverse the normal exchange reactions.

Ion exchange materials are unique in that their efficiency increases as the concentration of the solution decreases. For many exchangers, most efficient operation is obtained at concentrations in the order of one thousandths of a percent. Most applications, though, are made in solutions containing considerably higher concentrations than this. Coste[3] has shown that ion exchange resins will remove aluminum and iron effectively from solutions of up to 10 pct chromic acid.

Ion Exchange Resins

Ion exchange resins are insoluble, porous, resinous structures to which active groups have been attached. Active groups such as $(-SO_3)^-$ and $(COO)^-$ pick up cations; hence structures saturated with groups such as these are called cation exchangers. Structures saturated with groups such as $(-NH_3)^+$ which pick up anions, are referred to as anion exchangers.

The resinous structure of necessity is resistant to strong acids, bases, oxidizing, and reducing agents, and most of the common organic solvents. An idea of the stability can be gaged from the fact that resins last for many years under constant use without detectable chemical or physical breakdown.

The ion exchange reaction is not confined to the surface of these synthetic resins. Its porous structure permits active groups in the center of a particle as well as those on the surface to remove ions. A high capacity resin such as Amberlite IR-120 will remove up to 3.3 lb Cu per cu ft of resin.

In this investigation several approaches to the problem of separating copper from zinc by ion exchange were considered. First, if a reagent could be found which would complex one of these metals and not the other, then by passing this reagent through a bed of exchanger containing copper and zinc, the

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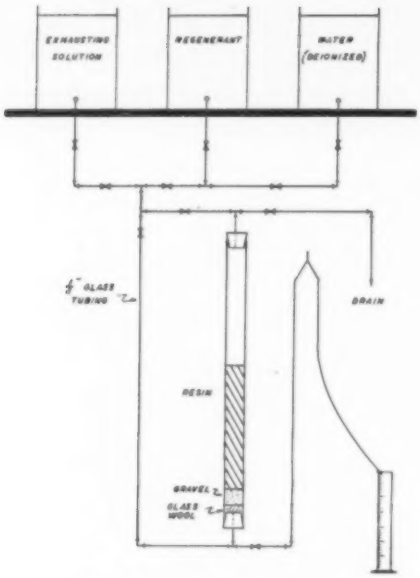

Fig. 1—Laboratory apparatus for ion exchange experiments.

metal that was complexed would be removed selectively. The rare earth metals have been separated in this manner.

Second, if an ion could be found which would replace only one of these two metals on the resin, then a separation could be made by eluting with a solution of that ion.

Third, if either copper or zinc could be complexed to an anion, then that anion could be picked up with an anion exchanger and the remaining cation could be removed with a cation exchanger.

Fourth, if the active groups of an ion exchange resin exhibited a strong preference for copper or zinc, then the two metals could be separated merely by passing a mixture of them through a column of exchanger.

Of these four possible methods for separating copper and zinc, the last one was considered to be the most practical. Accordingly, this study was limited to the investigation of the fractionation of copper and zinc by Method 4 on the two main types of cation exchangers commercially available.

Equipment and Materials

Fig. 1 shows the apparatus used. The glass column containing the resin was 2.50 cm in diam and 100 cm long. The resin bed was supported by a layer of glass wool covered by 4 in. of 28-mesh Ottawa sand. The tubing and pinch valves were so arranged that the solutions in any of the reservoirs could be delivered to the upper or lower end of the column.

The effluent was removed by first bringing it back up to an open Y above bed level. The open Y served to prevent the bed from siphoning dry if the influent solution should become exhausted.

The fractionation of copper and zinc on the two types of cation exchangers, Amberlite IR-120 and Amberlite IRC-50, was studied. Amberlite IR-120 is a high capacity nuclear sulphonic-acid type ion exchanger, produced in the form of bead-like particles. It can withstand strong acids and bases even at high temperatures.

In this investigation Amberlite IR-120 was used in the hydrogen form. The sodium form of the resin was converted to the hydrogen form by treatment with 10 pct sulphuric acid. The exchange reaction with copper and zinc for this resin is:

$$Cu^{++} + 2\ HSO_3R \rightleftarrows 2H^+ + Cu(SO_3R)_2$$

Amberlite IRC-50 derives its exchange activity from carboxylic acid groups. It exhibits exceptionally high capacities in basic solutions and is regenerated efficiently with acids. This resin is supplied in the hydrogen form. On conversion to the sodium form it undergoes up to 100 pct expansion. To allow for this expansion the conversion from the hydrogen to the sodium form was accomplished by stirring sodium hydroxide into a slurry of resin and water. Since the hydrogen form of Amberlite IRC-50 has a slow exchange rate, several hours were allowed for equilibrium to take place. The exchange reaction with copper and zinc could be represented as:

$$Cu^{++} + 2NaOOCR \rightleftarrows 2Na^+ + Cu(OOCR)_2$$

$$Zn + 2NaOOCR \rightleftarrows 2Na^+ + Zn(OOCR)_2$$

Procedure

Ion exchange operations are very simple since a run usually consists of only four steps: Exhaustion, regeneration, rinse, and backwash. This procedure was followed in all experiments.[4,5]

A typical experiment involved: 1—Exhaustion: The influent, consisting of an aqueous solution of copper and zinc, was passed through the column until the breakthrough point was reached; that is, the point at which traces of copper or zinc began to appear in the effluent. Periodic qualitative analyses were made to determine this point. After the breakthrough, the run was continued and the effluent was analyzed for copper and zinc. The curve resulting from a plot of zinc and copper concentration vs. volume of effluent was used to evaluate fractionation. These effluent curves will be discussed in some detail later. 2—Regeneration: The copper and zinc were removed from the saturated resin by passing a suitable amount of regenerating solution through the bed. With Amberlite IR-120, 10 pct sulphuric acid was used as the regenerant. Amberlite IRC-50, due to its inefficient exchange of copper for sodium, was regenerated in two steps. First, the copper and zinc were removed with 10 pct sulphuric acid and then the resin was converted back to the sodium form with 4 pct caustic. 3—Rinse: Water was passed through the bed until no more regenerant ions appeared in the effluent. 4—Backwash: In order to reclassify the resin and remove foreign matter, water was passed upflow through the column for 10 min. The flow rate was regulated to give a 75 pct bed expansion. The resin then was ready for the next cycle.

A colorimetric method of analysis was used for copper. For zinc the potassium ferrocyanide method employing uranyl nitrate as an external indicator was used.[6] Distilled water was employed for all backwashing and rinsing operations.

Experimental Results

The separation of copper from zinc using both resins—Amberlite IRC-50 and Amberlite IR-120—

was studied as a function of: 1—Flow rate, 2—pH, 3—concentration, and 4—copper-zinc ratio. In the study of these variables, the sodium form of Amberlite IRC-50 and the hydrogen form of Amberlite IR-120 were used.

One of the most promising features of ion exchange is the high ratio of concentration which can be achieved. To demonstrate this a 0.005 N $CuSO_4$ solution was concentrated on the carboxylic resin.

Amberlite IRC-50 vs. Amberlite IR-120: A very good fractionation of copper and zinc on the carboxylic resin, Amberlite IRC-50, was achieved. On the sulphonic resin, Amberlite IR-120, only a slight fractionation was obtained. In Figs. 2 and 3 the effluent curves for these two resins are given.

All of the zinc and copper were removed from the influent, and the sodium that was liberated passed on through the column. The amount of sodium appearing in the effluent was equivalent to the sum of zinc plus copper in the influent. As more influent passed over that part of the resin already exhausted, the copper in solution displaced the zinc. The displaced zinc then passed down the column and reacted with the first sodium resin with which it came in contact. This resulted in banding of the copper and zinc.

After 16 liters had passed through the column, the zinc had reacted with all of the sodium form of the resin. The column was then divided into two bands, the upper half contained copper and the lower zinc. This was visible inasmuch as the copper color on the resin had progressed only half way down the column when zinc first appeared in the effluent.

When the resin became saturated with zinc, further zinc entering the column plus that displaced by the copper appeared in the effluent. The stoichiometric displacement of zinc by copper was evidenced by the fact that the zinc in the effluent at 22 liters was equal to the sum of the zinc plus copper in the influent. At 42 liters the column contained mostly copper—94 pct. Beyond 42 liters practically no further reaction took place between the influent and the resin.

The exchange mechanism for the sulphonic resin, Fig. 3, was similar to that of the carboxylic resin; however, both ions traveled down the column at approximately the same rate.

To evaluate these effluent curves quantitatively, the percentage recovery and percentage purity of zinc in the effluent was plotted against effluent volume. To arrive at the percentage recovery and purity, the areas under the effluent curves were measured and multiplied by an appropriate factor to give the grams of metal appearing in the effluent. Knowing the influent volume and concentration, the percentage recovery and purity could be calculated at any given volume. Thus:

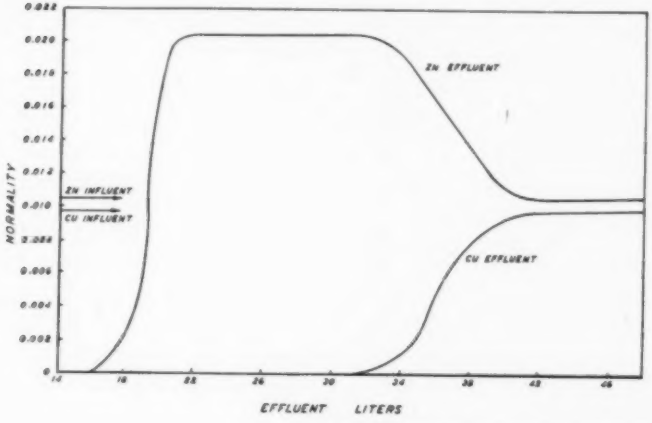

Fig. 2 — Fractionation of copper and zinc on Amberlite IRC-50, sodium cycle. Flow rate 0.005 ml per ml resin per min.

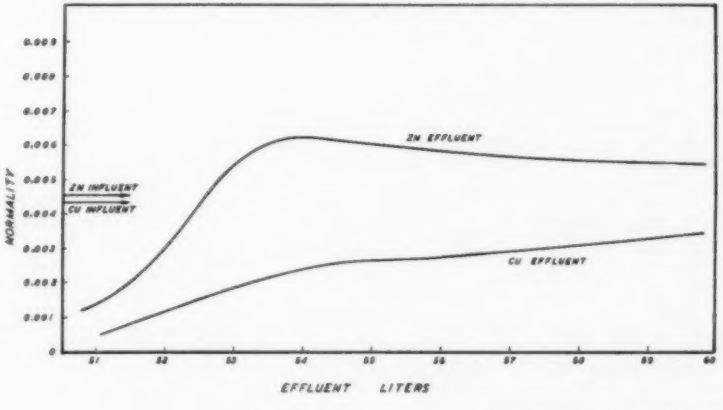

Fig. 3 — Fractionation of copper and zinc on Amberlite IR-120, hydrogen cycle. Flow rate 0.11 ml per ml resin per min.

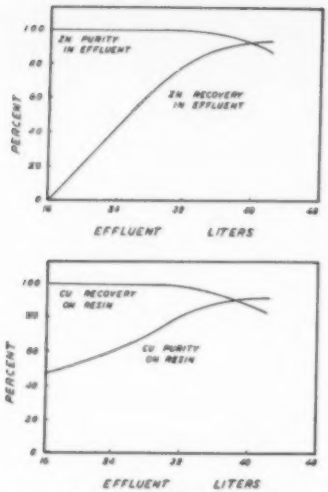

Fig. 4—Separation of copper and zinc on Amberlite IRC-50, expressed as percentage purity and recovery vs. volume of effluent.

$$\text{Recovery} = \frac{\text{Zinc recovered in effluent}}{\text{Total zinc to column in influent}} \times 100$$

$$\text{Purity} = \frac{\text{Zinc in effluent}}{\text{Zinc} + \text{Copper in effluent}} \times 100$$

In Fig. 4 the fractionation of copper and zinc on Amberlite IRC-50 is expressed in terms of zinc recovery and purity in the effluent. The effectiveness of this carboxylic resin in separating copper from zinc is indicated by the fact that 92 pct of the zinc was recovered in the effluent at a purity of 94 pct. Just as the purity and recovery of zinc in the effluent was increased, so the purity of the copper retained on the resin was increased over that in the influent. These results indicate that the carboxyl groups of Amberlite IRC-50 show a great preference for copper over zinc.

Amberlite IR-120 brought about a slight enrichment of zinc in the effluent. Apparently the sulphonic groups of this resin exhibit only a slight preference for copper.

Except for the effect of pH, the ensuing discussion will be limited to the performance of Amberlite IRC-50.

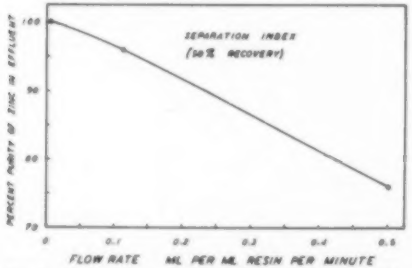

Fig. 5—Effect of flow rate on separation. Amberlite IRC-50, sodium cycle.

Effect of Flow Rate: The flow rate had a great effect on both the fractionation and capacity of the resin. The effectiveness of Amberlite IRC-50 was reduced at higher flow rates. In Fig. 5 the decrease in fractionation due to an increase in the flow rate is illustrated. The separation index used in this figure represents the percentage purity of zinc in the effluent when 50 pct of the zinc had been removed from the column. At a flow rate of 0.005 ml per ml of resin per min, a high degree of fractionation was obtained.

An increase in flow rate also impaired the capacity. At a flow rate of 0.1 ml per ml of resin per min the capacity was 0.22 g Cu per ml of resin compared to a capacity of 0.41 g Cu per ml of resin at a flow rate of 0.005 ml per ml of resin per min.

The effect of flow rate is due to the slow reaction rate between the carboxyl groups and copper and zinc. At high flow rates the copper and zinc ions are rushed through and do not have time to approach equilibrium conditions.

Effect of pH: Changes in pH had little effect on the fractionation of copper and zinc. It did, as mentioned, greatly affect the capacity of Amberlite IRC-50. In Fig. 6 the effect of pH on the two resins is illustrated. The effect of pH on Amberlite IR-120 was observed by varying the pH of the solution passing through the resin. With Amberlite IRC-50 the pH was varied by titrating NaOH into the acid form of the resin until the desired pH was reached. The influent pH was 5.0 in all cases. These curves mean

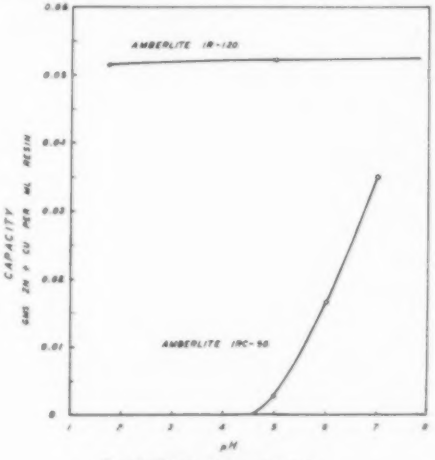

Fig. 6—Effect of pH on capacity.

that Amberlite IR-120 can be used effectively at a pH down to and below 1.75. Amberlite IRC-50 on the other hand is very sensitive to pH. To treat solutions with a lower pH, this carboxylic exchanger should be fully regenerated using caustic. Amberlite IRC-50 acts like a weak acid; consequently it has a very high affinity for hydrogen ions. Amberlite IR-120 acts like a strong acid which is highly ionized; its affinity for hydrogen is low.

Effect of Concentration and Copper-Zinc Ratio: At a copper to zinc ratio of 1:1, variation in total concentration of copper and zinc between 0.01 and 0.1 normal had no effect on the fractionation of copper and zinc. Below a normality of 0.01 the fractionation,

if any change occurs, should improve. At what concentration above 0.1 normal the efficiency of the resin falls off was not determined.

The copper-zinc ratio, however, had a decided effect on the fractionation. Below a copper to zinc ratio of 1:1, copper was removed effectively from a solution of copper and zinc. On the other hand, as the ratio of copper to zinc increased above one, the complete removal of copper became more difficult. The good fractionation obtained at lower copper-zinc ratios indicates that it would be possible to remove traces or small amounts of copper from stronger solutions of zinc.

Exchange Resins as Concentrators

The experiment to demonstrate exchangers as concentrators was made by passing an 0.005 N $CuSO_4$ solution over a bed of Amberlite IRC-50 until the copper breakthrough in the effluent was reached. A 40 pct H_2SO_4 eluting solution then was passed through the column and analyzed for copper. The elution curve is given in Fig. 7. Shortly after 100 cc of eluting solution had passed through, the solubility of $CuSO_4$ was exceeded which resulted in the precipitation of $CuSO_4$ in the ion exchange bed. The gradual decrease in concentration of copper towards the end of the elution probably was caused by the copper sulphate crystals going back into solution.

The ratio of concentration vs. percentage recovery for this experiment is given in Fig. 8. When 90 pct of the total copper had been recovered in the effluent,

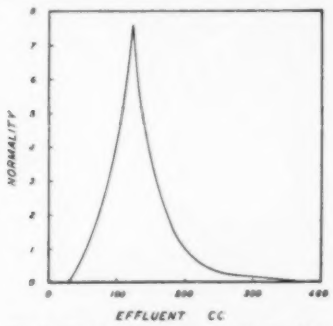

Fig. 7—Elution of copper from Amberlite IRC-50 using 40 pct H_2SO_4.

the volume ratio of concentration was 625.

The high avidity of Amberlite IRC-50 for hydrogen ions makes very high ratios of concentration such as this possible. The regeneration efficiency using acids approaches 100 pct in most cases. That is, almost 100 pct of the hydrogen ions in the regenerating solution contribute to the replacement of copper ions on the resin. On the sulphonic type resins approximately 35 pct of the hydrogen ions in an acid regenerating solution are actively engaged in the exchange reactions.

Conclusions

It is possible by means of ion exchange resins to remove metal ions from very dilute solutions and recover them in a concentrated form. This suggested the use of ion exchange in metallurgical recoveries. A survey of the literature revealed that little had been done in applying ion exchange to metallurgical problems. Although removal of ionic impurities has been investigated extensively in connection with

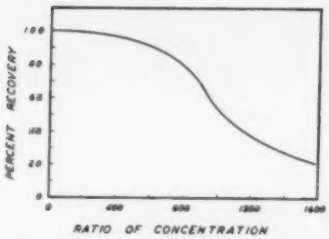

Fig. 8—Ratio of concentration vs. recovery with Amberlite IRC-50 used as a concentrator.

water softening, only limited work has been done on metal separations.

Since the metallurgist is concerned with the separation of metals as well as their concentration, an investigation of the selectivity of ion exchange resins was undertaken. The results of this work on the separation of copper from zinc may be summarized as follows:

1—A carboxylic-type resin can be used to effect the recovery of copper from a mixture of copper and zinc ions. The capacity of this type of resin was very high above a pH of 7; however, below a pH of 5 the capacity became too low for most uses. Consequently, the carboxylic resin would be advisable where a separation is desired.

2—A low degree of selectivity was obtained on the sulphonic resin. It did exhibit a high capacity under wide variation of pH and flow rates; therefore, this type of resin would be useful for the removal of ions under acidic conditions.

3—Ion exchange resins, especially the carboxylic type, can be used to concentrate ions from very dilute solutions.

It appears that there are several possible uses for ion exchange resins in metallurgy. They seem particularly suited to the recovery of metal ions from waste waters. Not only would the recovered metal be of value, but stream pollution could be prevented and possibly the water could be reclaimed.

What role ion exchange will play in the metallurgical field remains to be seen. It seems likely that through this unit process the range of metal recovery can be extended far beyond that obtainable by conventional methods.

Acknowledgment

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Ignition Temperatures of Magnesium And Magnesium Alloys

by

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Leonard B. Gulbransen
John R. Lewis
and
J. Hugh Hamilton

A simple reproducible method was developed for determining the ignition temperatures of magnesium and magnesium alloys and by this method magnesium and over 100 magnesium alloys were measured. The ignition temperature of magnesium was determined in O_2-SO_2, O_2-N_2 mixtures and in O_2 from 0.166 to 10 atm pressure. The ignition temperature of magnesium is generally lowered by alloying and increased by an increase in oxygen pressure.

WITH the expanded use of magnesium alloys in industry, ignition temperatures are of considerable importance, especially in heat treating and for service at elevated temperatures. Magnesium alloys exhibit a relatively slow linear oxidation rate up to temperatures near the melting point.[1] At some critical temperature the rate of oxidation becomes extremely rapid. This high rate of oxidation is accompanied by the emission of light and additional characteristics suggesting a flame.

The literature concerning the ignition temperatures of magnesium and magnesium alloys is relatively incomplete and the values reported by various authors are not in agreement. The most probable reasons for this are: 1—The absence of a suitable definition of ignition, and 2—the need of a standardized method of determining the ignition temperatures of inflammable metals and alloys.

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The exact date of the discovery of the fact that magnesium will ignite and burn is unknown. It is likely that H. Davey encountered this property of the metal during its preparation in 1808. The first reference in the literature specifically on ignition of magnesium is by Lenze, Metz, and Rubens.[2] They investigated the inflammability of certain magnesium alloys. Brown[3-4] reported that magnesium ribbon will ignite in air at 507°C by what was called the rising temperature method. Hartman, Nagy, and Brown[5] reported that magnesium powder ignites from 475° to 560°C depending on particle size. According to Guise, Mars, and Wilson[6] prolonged heating in air at 427°C of common casting magnesium alloy causes it to ignite. Samples of magnesium alloys were placed directly in the flame of a torch by Carapella and Shaw.[7] These investigators obtained some evidence of melting prior to ignition. For commercial magnesium, they reported an ignition temperature of 650°C. Their values varied from 450° to 800°C for magnesium alloys. Willmore and Peterson[8] studied the effect of air velocity, humidity, rate of heating, and foreign metal contact on the ignition temperature of magnesium. They conclude that melting is not a prerequisite for ignition and that the conditions which influence ignition are complex and difficult to analyze.

The only quantitative theoretical treatment of the ignition temperatures of magnesium and magnesium

alloys is that of Eyring and Zwolinski.[9] Following the ideas set forth by Pilling and Bedworth[10] in their discussion of the ignition of calcium metal, Eyring and Zwolinski concluded that a metal sample will ignite if the conduction of heat through the oxide film is insufficient to remove the heat produced at the metal oxide interface as a result of the oxidation reaction.

Actually, Constable,[11] Suzuki,[12] and others have shown that this condition exists at temperatures below the ignition temperature.

Eyring and Zwolinski state that as a result of inadequate loss of heat through the film, the temperature at the metal-oxide boundary will increase, accelerating the rate of the reaction. The progressive acceleration of the rate of oxidation will result in the vaporization of magnesium with subsequent ignition of the metal vapor.

The thermal energy lost by conduction from the sample can be equated to the thermal energy produced by the oxidation of the sample. This relationship is expressed by the equation:

$$\varkappa \frac{(T - T_o)}{d} = \frac{\Delta H}{N} v \qquad [1]$$

where $\varkappa$ is the thermal conductivity, v is the rate of oxidation, T is the temperature at the metal-oxide interface, T_o is the temperature at the outer surface of the film, d is the thickness of the oxide film, ΔH is the heat of formation, and N is Avogadro's number. According to the proposed theory[9] ignition will occur at the instant the thermal balance represented by eq 1 is destroyed.

The reaction rate, v, from the Theory of Absolute Reaction Rates[13] may be written as:

$$v = C_s \frac{kT}{h} e^{-\epsilon/kT} \qquad [2]$$

where C_s is the number of adsorption sites on metal atoms per sq cm, k is Boltzmann's constant, h is Planck's constant, T is the temperature °K, ϵ is the activation energy. Substituting eq 2 in eq 1 it becomes:

$$\varkappa \frac{(T - T_o)}{d} = C_s \frac{kT}{h} e^{-\epsilon/kT} \frac{\Delta H}{N} \frac{AM}{AF} \qquad [3]$$

where AM/AF represents a roughness factor. Rewriting eq 3 in a more convenient form:

$$T_o = \left(1 - C_s \frac{kd\Delta HF}{\varkappa h N} e^{-E/RT}\right) T \qquad [4]$$

and substituting in the following values in eq 4:

C_s = 1.1×10^{15} Mg atom per sq cm
k = 1.38×10^{-16} ergs per °K
ΔH = 146 kg-cal per mol
F = AM/AF = 16
h = 6.62×10^{-27} erg sec
$\varkappa$ = 2.8×10^{-4} cal cm °C^{-1} cm^{-2} sec^{-1}
N = 6.02×10^{23} atoms per mol
E = 42.7 kg-cal per mol for 1.78 pct Al-Mg alloy, from ref. 1.
E = 50.5 kg-cal per mol for Mg from ref. 1.

Eyring and Zwolinski calculated the values for the ignition temperature of magnesium shown in Table I.

Thus, the theory of Eyring and Zwolinski indicates that the ignition temperature is dependent on the oxide film thickness. As will be shown later, this theory does not agree with the experimental results obtained by the authors in that the time delay experiments indicate that the ignition temperature of magnesium is independent of the nonprotective oxide film thickness. In addition, the thermal equilibrium represented by eq 1 is violated at temperatures below the ignition temperature. The Constable effect would be impossible under the imposed conditions of this equation. As will be shown later, this theory does not explain satisfactorily the experimentally observed fact that the ignition temperature of magnesium is pressure dependent.

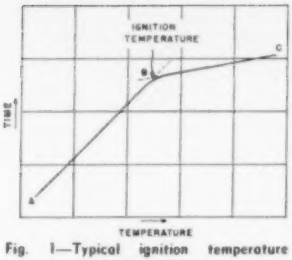

Fig. 1—Typical ignition temperature determination.

From the literature pertaining to the ignition temperatures of magnesium and magnesium alloys, as cited above, it is obvious that none of the experimental values agree and that there is some conflict as to the exact definition of the ignition temperature.

Experimental Procedure

In this investigation, the ignition temperature is defined as the "explosion temperature," that is, the temperature at which the rate of oxidation suddenly becomes extremely rapid and a "flame" appears. From preliminary experiments it was found that the following method was satisfactory for determining the ignition temperature of magnesium and magnesium alloys. A thermocouple was placed in intimate contact with a small magnesium sample. The sample was heated in an electric furnace at a specified rate in an oxygen atmosphere. The heating curve of the sample shows two distinct branches. A typical curve is shown in Fig. 1. Branch a-b corresponds to the heating of the sample by the furnace and b-c to the heating of the sample by ignition.

From actual observation, it was found that the point b corresponds very nearly to the temperature at which a flame is propagated. Point b then corresponds to the definition of ignition temperature. This definition was adopted because the values of the ignition temperatures are reproducible (i.e.,

Table I. Experimental Vs. Calculated (Eq 4) Ignition Temperatures of Magnesium and Magnesium Alloys

Alloy	Oxide Film Thickness, Cm	Calculated °C (Eq 4)	Experimental °C (Authors)
1.78 pct Al	1.35×10^{-9}	551	600*
3.81 pct Al	1.35×10^{-9}	480	582
Pure Mg	5×10^{-9}	642	623
Pure Mg	1×10^{-1}	618	623
Pure Mg	2×10^{-1}	593	623
Pure Mg	5×10^{-7}		623

* Leontis and Rhines[1] obtained a value of 548°C.

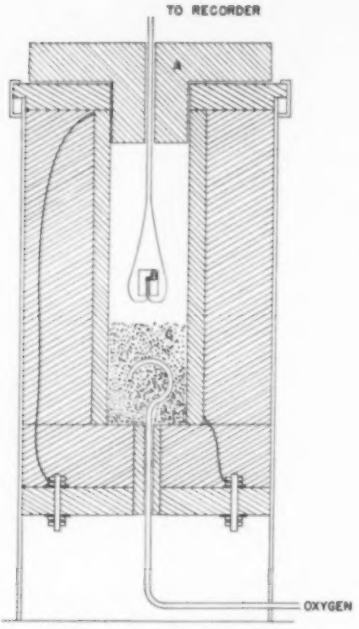

Fig. 2—Furnace used in ignition temperature experiments.

±5°C) on any given alloy composition. In addition, the ignition temperature is not influenced by complicating factors such as the Constable effect[11] ("self heating" of the sample); size of sample, within reasonable limits; rate of flow of oxygen; time of exposure; and rate of heating.

Measurement of Ignition Temperature

The alloy samples were melted in a small induction furnace, cast in a preheated split steel mold (½ in. diam x 3 in.) and turned on a lathe to 0.375 in. and cut into ½ in. lengths. Power cross feeds of 0.0018 in. per revolution were used to insure uniform surface conditions on all samples. A hole was drilled coaxially ⅜ in. deep with a No. 47 wire gage drill to provide a well for the thermocouple.

The hot junction of the thermocouple was inserted into the well of the alloy sample to be tested and the lead wires doubled back to form a U-shaped cradle so that only the junction was in contact with the sample.

Throughout the investigation the ignition temperatures were determined by measuring the temperature of the sample with a chromel-alumel thermocouple (28 gage) connected to a Leeds and Northrop Micromax recorder.

The schematic arrangement of the furnace (Hoskins Type FA120) with the sample in position is shown in Fig. 2. This equipment was used in all ignition temperature determinations in oxygen, oxygen-nitrogen, and oxygen-sulphur dioxide mixtures at atmospheric pressure.

With the sample in position, the flow of pure oxygen or oxygen mixture was started through the bottom of the furnace and adjusted to a rate of 250 ml per min. (The ignition temperature of pure magnesium was found to remain constant at flow rates from 50 to 500 ml per min.)

After 5 min the furnace was turned on (voltage to furnace held constant at 100 v, i.e. 83 pct rated voltage). Heating was continued until the recorder showed a sharp increase in rate of temperature rise, indicating ignition. After completion of the test, the tangential intersection of the two branches of the heating curve was plotted and the temperature of ignition evaluated.

Oxygen was used for the majority of the ignition temperature determinations. While this does not duplicate the conditions during heat treatment, it does provide comparative results between magnesium and its alloys. When air was substituted for oxygen, somewhat erratic temperatures were obtained, but with oxygen no such difficulty occurred and usually the mean variation did not exceed 2°C.

The ignition temperatures of the following systems have been determined: Mg, Mg-Ag, Mg-Bi, Mg-Co, Mg-Ca, Mg-Ni, Mg-Sb, Mg-Pb, Mg-Zn. In addition a number of other binary alloys have been studied in certain regions as well as a number of

Table II. Ignition Temperatures of Magnesium and Magnesium Alloys in Oxygen at Atmospheric Pressure

Composition, Pct Alloying Element	Ignition Temperature, °C	Composition, Pct Alloying Element	Ignition Temperature, °C	Composition, Pct Alloying Element	Ignition Temperature, °C
Pure EMCO Mg	623	Mg-Ca		Mg-Zn	
		1.0	624	19.07	523
Mg-Al		2.0	630	19.33	530
5.67	558	5.0	633	19.91	552
5.88	527			30.14	513
11.43	530	Mg-In		30.2	534
13.97	535	10.0	613	31.74	524
18.17	502	20.0	593	33.48	524
26.04	514	30.0	586	51.13	588
33.25	513			60.72	542
38.65	560	Mg-Li		69.73	535
53.7	535	0.3	553	76.9	541
63.15	462	0.8	578	89.33	538
80.33	None	4.0	513		
82.72	to	8.0	514	Mg-Al-Zn	
93.73	900	11.4	518	1.21 Al	610
				1.12 Zn	
Mg-Ag		Mg-Mn			
4.8	550	1.0	621	2.16 Al	585
9.04	537	2.0	616	2.07 Zn	
14.12	540	3.0	631		
				3.14 Al	575
		Mg-Ni		3.27 Zn	
		5.0	510		
Mg-Bi		10.0	517	4.23 Al	544
10.0	500	20.0	508	4.19 Zn	
20.0	548				
		Mg-Sb		3.18 Al	576
		1.20	582	4.98 Zn	
Mg-Cd		4.38	585		
7.15	612	5.22	588	5.95 Al	560
8.35	597	9.0	588	3.58 Zn	
10.78	588	21.6	593		
12.54	593	29.1	586	6.10 Al	543
14.07	595			6.02 Zn	
15.75	603	Mg-Si			
17.86	587	1.83	610	10.69 Al	549
20.98	596	3.15	625	14.26 Zn	
23.05	587				
25.31	607	Mg-Sn		Mg-Al-Cd	
30.71	584	9.88	576	14.75 Al	534
33.19	578	10.52	580	11.26 Cd	
35.10	596	11.34	556		
41.17	571	20.33	571	9.5 Al	544
44.09	559	22.31	574	4.98 Cd	
50.93	541	25.62	574		
61.40	517			Mg-Cd-Ag	
62.30	522			22.9 Cd	570
71.80	535	Mg-Pb		0.33 Ag	
80.73	533	16.24	575		
90.53	551	29.97	565	13.3 Cd	560
		45.98	553	1.77 Ag	
		58.26	504		
Mg-Co				24.9 Cd	592
1.0	617			2.22 Ag	
5.0	616	Mg-Zn			
		3.04	595	26.77 Cd	587
		4.81	552	2.3 Ag	
Mg-Cu		5.23	546		
10.3	537	9.25	509	Mg-Cd-Zn	
20.5	519	10.34	537	19.9 Cd	553
30.76	532	12.5	558	2.78 Zn	

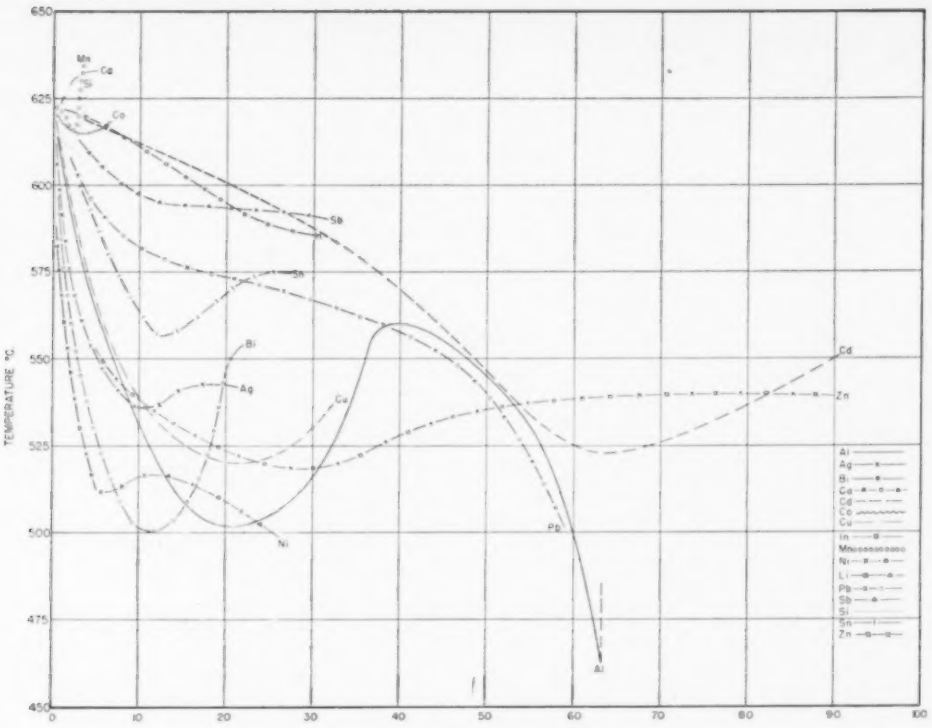

Fig. 3—Effect of alloying elements on the ignition temperature of magnesium.

ternary and quaternary alloys of specific compositions. The results are shown in Table II and summarized in Fig. 3.

The results obtained for magnesium in oxygen-nitrogen mixtures are shown in Table III. The ignition temperatures of magnesium in mixtures of oxygen and sulphur dioxide are given in Table IV.

Table III. Ignition Temperatures of Magnesium in Oxygen-Nitrogen Mixtures

O, Pct	N, Pct	Ignition Temperature, °C
89.5	10.5	649 629 629
80	20	635 632
70	30	641 638
60	40	627 629
50	50	632 632
40	60	627 627 604
30	70	627 627
20	80	638 613 624 635
10	90	638 635 616

Table IV. Ignition Temperatures of Magnesium in Oxygen-Sulphur Dioxide Mixtures

O, Pct	SO_2, Pct	Ignition Temperature, °C
100	0	623
99.5	0.5	630
99.25	0.75	638
99.0	1.0	646
97.0	3.0	648
96.0	4.0	649
94.2	5.8	648

Delayed Ignition of Magnesium Below Normal Ignition Temperature

As pointed out above, the theory of ignition of magnesium as proposed by Eyring and Zwolinski[9] indicates that the ignition temperature is dependent upon the thickness of the oxide film on the sample. The following series of experiments were conducted to determine the validity of this theory.

Experimental Procedure: Preliminary experiments on the ignition of magnesium with prolonged heating showed that the Constable effect[11] (a spontaneous rise in temperature as a result of heat evolved by the oxidation process) may occur at temperatures considerably below the ignition temperature. Due to this spontaneous rise in tempera-

Table V. Time Necessary for Magnesium to "Self Heat" to the Temperature of Ignition

Sample Number	Constant Furnace Temperature, °C	Sample Temperature at Which Ignition Occurred	Time Interval to Ignition Temperature, Min
1	623	623	0.00
2	602	623	34' 26"
3	587	623	213'

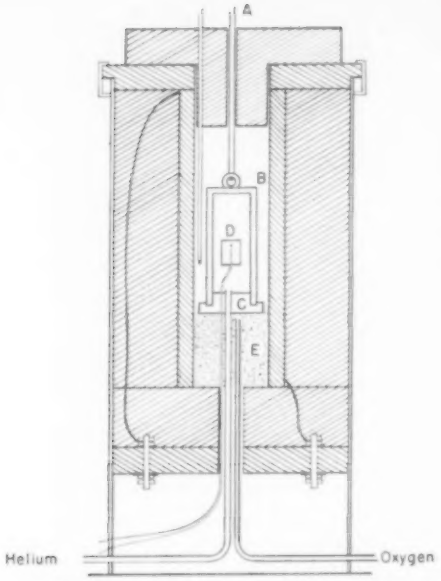

Fig. 4—Furnace and bell used in time delay experiments.

ture, it is necessary to control the temperature of the furnace or bath by a thermocouple in the furnace wall or very near to it. Also, the sample temperature must be measured by a separate thermocouple, since its temperature will be above the furnace temperature at any finite time after the introduction of oxygen.

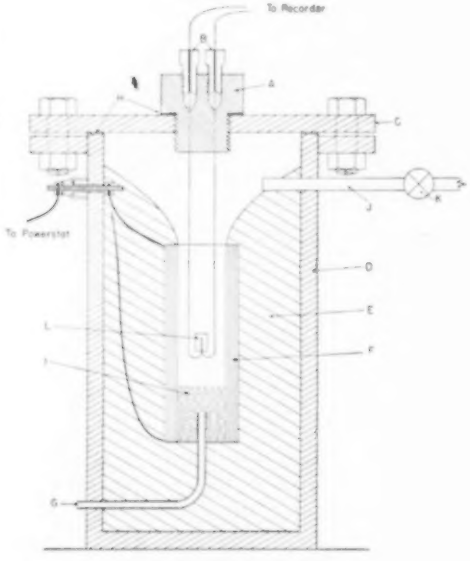

Fig. 5—Pressure ignition furnace.

The equipment used to conduct these experiments was designed to avoid the possible difficulties from the Constable effect. The apparatus is shown schematically in Fig. 4.

The furnace was a Hoskins Type FA 120, the same type as used in the standard ignition determination. The furnace temperature was controlled by means of a thermocouple placed very near the furnace wall and connected to a Leeds and Northrop Micromax temperature controller. The bottom section of the heating chamber was filled with Ottawa sand, *E*, to allow the incoming gases to reach the furnace temperature. A small circular base plate of stainless steel, *C*, was fitted with the sample thermocouple and the sample, *D*, and made so that the bell, *B*, was placed in the sealing ring of the base plate completely covering the magnesium sample. While the furnace was cold, the helium* flow into the interior of the bell was started to prevent oxidation and continued until temperature equilibrium between the sample and the furnace walls was reached. At the same time oxygen was passed into the heating chamber. When equilibrium was established, the flow of helium was stopped and the bell raised to allow the oxygen to come in contact with the magnesium sample. Time was counted from this instant. When ignition occurred the elapsed time interval was recorded. The results of these experiments are shown in Table V.

Change in Ignition Temperature of Magnesium as a Function of Oxygen Pressure

The object of these experiments was to determine if the ignition temperature is a function of oxygen pressure. These data may indicate the type of reaction involved in ignition of the magnesium sample.

Experimental Procedure: The procedure for determining the ignition temperature using the special pressure furnace, Fig. 5, is as follows: The thermocouple wires were led through the threaded steel plug, *A*, and the packing glands, *B*. The packing, moistened asbestos fiber, was placed in the conical wells in plug, *A*, and the gland nuts, *B*, screwed into place. The sample, *L*, was suspended by the thermocouple wires and the assembly screwed into the furnace top, *C*, sufficiently tight to seal, *A* and *C*, by means of the lead gasket, *H*. Oxygen was then admitted through the inlet tube, *G*, from the oxygen cylinder via a reduction valve which reduced the pressure to a maximum of 200 psi.

The oxygen passed through the Ottawa sand zone, *I*, and the sample chamber, *B*, of the electrically heated furnace, *F*. The valve, *K*, on the outlet pipe, *J*, was opened and closed intermittently until all air was purged from the system. Valve *K* then was closed and the pressure adjusted to the desired value. The thermocouple wires were connected directly to a Brown recording potentiometer. Heating was then started following the same program as for the standard ignition determination.

The data obtained in the study of the effect of oxygen pressure on the ignition temperature of magnesium is shown in Table VI and Fig. 6.

Lowering Ignition Temperature of Magnesium

The lowering of the ignition temperature of magnesium by contact with other metals has not been investigated thoroughly. Preliminary experiments

* Helium, special purity (no dew point). Furnished through the courtesy of S. R. Zimmerley, U. S. Bureau of Mines, Salt Lake City.

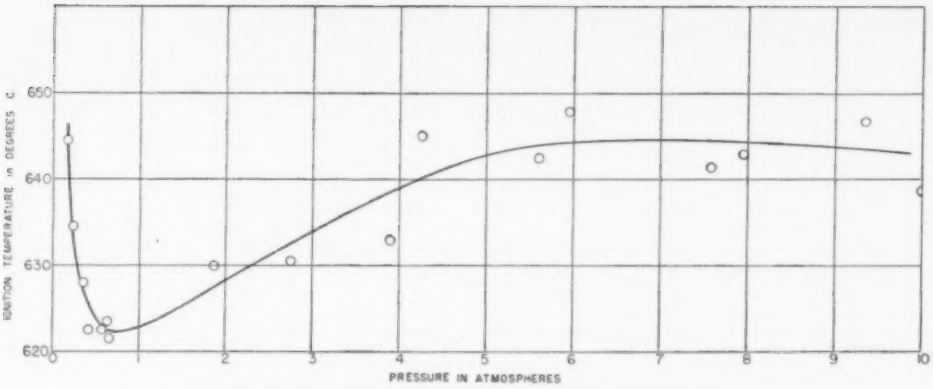

Fig. 6—Ignition temperature of magnesium with respect to oxygen pressure.

performed in this laboratory indicate that the ignition temperature of magnesium is lowered appreciably by contact with aluminum, nickel, and 70-30 brass. Silver and plain carbon steel did not affect the ignition temperature. The samples were prepared by drilling a hole through a piece of pure magnesium followed by reaming with a 2/0 taper pin reamer. The dissimilar metal in the form of a pin was driven in and the ends turned off thus giving a perfect contact. The values of the ignition temperatures of pure magnesium in contact with other metals are presented in Table VII (oxygen atmosphere).

Discussion of Results

The method developed for the determination of the ignition temperatures of magnesium and magnesium alloys is simple and reproducible. As an illustration of the accuracy of this test, ten samples of magnesium of the same lot were run in oxygen by four different individuals over a period of six months. The average ignition temperature obtained from this series of tests was:

$$623^{\circ}C \pm 0.5^{\circ}C$$

The ignition temperature of magnesium generally is lowered by the addition of alloying elements providing the melting point (liquidus) is lower than pure magnesium. Ignition of magnesium alloys may occur at temperatures either above or below the melting point indicating that the conclusions of Carapella and Shaw[5] are not generally valid. The Mg-Cd system, Fig. 3, is an excellent example of this effect. The melting point of the alloy has some influence on the ignition temperature, but it is not the only factor that must be considered. This is discussed in detail in ref. 14.

One rather unusual observation was made of the magnesium and magnesium alloy samples just prior to ignition. Normally the oxide coating present is white in color. However, just an instant before ignition occurs, the oxide coating turns a dark brown or black color. Once the color change occurs, ignition follows immediately.

A correlation exists between the rates of linear oxidation and the ignition temperatures of magnesium alloys. Sufficient data to justify its presentation is available only on the Mg-Al system. Qualitatively, however, all of the alloy compositions investigated by Leontis and Rhines show the same relationship. Table VIII shows the correlation of the linear oxidation rates and the ignition temperatures of some Mg-Al alloys.

The ignition temperature of magnesium in oxygen-sulphur dioxide mixtures increases from 623°C at zero percent SO_2 to approximately the melting point of magnesium (650°C) at 1.7 pct SO_2. From 1 to 5.8 pct SO_2 no further increase is observed. Qualitatively, at least, it is well known that high concentrations of SO_2 prevent the ignition of magnesium at temperatures considerably above the melting point. Thus, a further increase in the ignition temperature would be expected at concentrations above 5.8 pct SO_2 which was the maximum concentration investigated in this work.

The results obtained on the time-delay of the ignition of magnesium show that if the furnace or bath

Table VI. The Ignition Temperature of Magnesium in Oxygen as a Function of Pressure

Oxygen Pressure, Atm	Ignition Temperature, °C	Average Ignition Temperature
0.166	643 645	644.5
0.234	636 633	634.5
0.365	628 628	628
0.43	622 623	622.5
0.58	623 622	622.5
0.64	623 624	623.5
0.688	621 622	621.5
1.0	10 at 623	623
1.865	630 630 629 631	630
2.75	633 628	630.5
3.9	635 631	633
4.25	645 645	645
5.6	644 641	642.5
5.95	649 647	648
7.68	641 642	641.5
7.95	641 644 644	643
9.35	647 647	647
10.0	640 638 638	638.8

Table VII. Ignition Temperatures of Magnesium in Contact with Other Metals

Sample	Contact Metal	Ignition Temperature, °C
Mg		623
Mg	Ni	588
Mg	Ag	623
Mg	70-30 brass	538
Mg	Steel	623
Mg	Al	523

Table VIII. The Relation of the Ignition Temperature to the Oxidation Rate of Mg-Al Alloys

Alloy, Pct by Wt	Oxidation Rate,* Mg per Sq Cm per Hr 475°C	Ignition Temperature, °C
Mg	0.01	623
Mg-1.78% Al	0.025	605
Mg-3.18% Al	0.051	580
Mg-7.23% Al	0.305	558
Mg-9.12% Al	7.7†	543
Mg-18.66% Al	17.0†	503

* Sources, ref. 1.
† Extrapolated.

is maintained at some constant temperature below the ignition temperature of magnesium in oxygen, the magnesium will autoheat to the ignition temperature. The ignition temperature obtained under the conditions imposed in the time-delay experiments is identical with the value obtained in the normal ignition temperature experiments.

The approximate thickness of the oxide films present on the samples listed in Table V may be calculated from the oxidation rate data of Leontis and Rhines and an approximate value for the density of the MgO film as 0.8 g per cc. The approximate thicknesses are: Sample 1, Table V, 5×10^{-7} cm; Sample 2, 1.56×10^{-6}; Sample 3, 5.5×10^{-6}. Thus the oxide film thickness changes by a factor of 10^{4} cm yet the ignition temperature remains unchanged. This is not in agreement with the predicted results of Eyring and Zwolinsky,[10] see Table I.

The results obtained on the change of ignition temperature of magnesium with respect to oxygen pressure conclusively prove that the ignition reaction of magnesium is oxygen pressure dependent. The ignition temperature of magnesium increases with an increase in total oxygen pressure from 1 to 10 atm pressure. Below atmospheric pressure, the ignition temperature decreases with a minimum at about 0.4 atm, rising again at lower pressures.

The theory of ignition of metals and alloys by Eyring and Zwolinski does not account for the effect of oxygen pressure on the ignition temperature. If eq 2 is used, adsorption on the activated sites is assumed. Under increased pressures the velocity of the reaction should increase causing a decrease in the ignition temperature. This, of course, is in direct contradiction to the experimental results of the authors on ignition and of the work of Leontis and Rhines[1] and E. A. Gulbransen[15] on oxidation of magnesium.

Dissimilar metal contacts generally lower the ignition temperature of magnesium by localized diffusion and alloy formation. This would cause a small zone in which the rate of reaction is increased, accompanied by a lowering of the ignition temperature. This result has also been obtained by Willmore and Peterson.[6]

Summary

A simple reproducible method of determining the ignition temperature of magnesium and magnesium alloys has been developed. This method was used to determine the ignition temperature of over 100 different magnesium alloys in oxygen at atmospheric pressure. The ignition temperature of pure magnesium was investigated in oxygen-nitrogen, oxygen-sulphur dioxide, and in oxygen from 0.166 to 10.0 atm pressure. The ignition temperature of magnesium generally is lowered by the addition of alloying elements. Ignition of magnesium alloys may occur either above or below the liquidus line. The ignition reaction of magnesium is pressure dependent, and hence any theory of ignition must satisfy this fact.

Acknowledgments

The authors wish to express their thanks to the Technical Command, Army Chemical Corps, whose sponsorship made this work possible. The authors also wish to express their gratitude for assistance given by M. A. Cook, Professor of Metallurgy, University of Utah, and by J. Blackledge, D. Richins and LeRoy Jackman, Graduate Students at the University of Utah.

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Correction

In the March 1951 issue: *Solubility of Hydrogen in Molten Lead* by W. R. Opie and N. J. Grant. P. 245, the second equation should read:

$$\text{Log}_{10}K = \frac{-\Delta H}{4.575\,T} + C$$

Rate of Sintering of Copper Under a Dead Load

by F. N. Rhines and H. S. Cannon

The application of a static load to a copper powder compact during sintering at an elevated temperature accelerates the rate of sintering in such a way that a given load induces the same proportional increase in rate for all times of sintering. It is shown that sintering under a load is like creep under a fixed load in that the stress required to accomplish a given degree of densification is proportional to the logarithm of the sintering time.

VIRTUALLY all of the theories of sintering that have been put forward within recent years have contained the assumption that the chief driving force of the process is the surface tension resident in the exposed surfaces and internal pores of the compact, or powder mass. An externally applied load might be expected to provide a somewhat equivalent driving force for sintering. It is known that the application of a compressive load, during sintering, hastens densification, but it is by no means clear whether sintering under the influence of surface tension alone and sintering under an applied load are fundamentally similar processes. The present study was undertaken in an effort to obtain an answer to this question and with the hope that the answer may contribute to an understanding of the mechanism of sintering. It has been found that there is a close relationship between sintering and creep processes.

Copper powder compacts were sintered in hydrogen at 1000°C under dead loads of 0 to 165 psi and the progress of sintering was observed by means of density measurements. Using a commercial reduced oxide copper powder, see Table I, cylindrical compacts ½ in. x ½ in. high were made at a pressure of 12,500 psi. For sintering, these were placed in a cylindrical graphite container into which they fitted snugly. A compressive axial load was applied to the compact through a graphite rod of similar diameter, which rested upon the upper end face of the compact; iron weights, in suitable amount, were placed upon the graphite rod to provide the load. This assembly was encased in a vertical silica tube within a resistance-type furnace capable of maintaining a substantially constant temperature within the working zone. After various predetermined times at temperature, the samples were removed from the furnace and their density was measured by conventional means. The heating-up and cooling-down times have been included in the computed sintering time, using the assumption that the sintering rate doubles for each increase of 10°C in temperature. The experimental results are presented in Table II.

Upon metallographic examination of the specimens, it was found that there was no apparent change in the shape of the pores as a result of loading, i.e. no flattening, Fig. 1. Substantial contraction away from the container walls was observed in all samples sintered with loads of 10.5 psi and less.

Table I—Analysis of Copper Powder

Mesh Number	Percentage
+150	0-1
+200	13.0
+250	4.6
+325	13.4
−325	68.9
Hydrogen loss, pct	0.19
Apparent density	2.47
Flow rate, sec	30.4
Fisher sub-sieve size	7.8

Table II—Density of Compacts Sintered under Load*

Load, Psi	Time, Hr	Density	Ideal Density, Pct
0	0	4.75	54.3
0	1	7.05	78.7
0	3	7.61	85.0
0	10	8.16	91.0
0	96	8.73	97.4
10.5	1	7.35	82.0
10.5	7	8.13	90.7
10.5	110	8.78	98.0
30	1	7.57	84.5
30	10	8.42	94.0
30	100	8.80	98.2
70.5	1	8.21	91.6
70.5	3	8.44	94.2
70.5	11	8.69	97.0
70.5	34	8.78	98.0
70.5	96	8.87	99.0
125	1	8.53	95.2
165	1	8.64	96.4

* Compacts prepressed at 12,500 psi. All sintering conducted at 1000°C in hydrogen.

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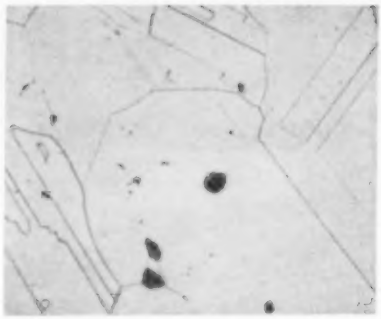

Fig. 1. Typical appearance of pores after 98 hr at 1000°C under a load of 70.5 psi, prepressed sample. X500.

A few experiments were made, also, using a loose powder fill in the graphite container. Again, the sintering temperature was 1000°C and the atmosphere was hydrogen. The results, shown in Table III, are similar to those for the sintering of prepressed powders except that longer times are required to attain a given density value under a given load. It is interesting that loose powder can be sintered to a density as high as 98 pct of the ideal, under a load as small as 115 psi, in as little as five days.

Discussion of Results

It is characteristic of sintering that the density approaches its ideal value for massive metal at a continually decreasing rate, so that complete densification is not attained within experimentally feasible times. This is seen to be true, also, when a moderate load is applied. The rate of densification is increased by loading, but within the range of loads here employed, the final approach to the ideal density is very gradual and full densification has not been attained. That sintering progresses under load in the same manner as without load is shown by Graph A, Fig. 2, wherein the "densification parameter", α, is seen to be independent of time. The "densification parameter" is the ratio of the change in the percentage of porosity due to loading (at fixed time) to the percentage of porosity (at the same time) when no load has been applied:

$$\alpha = \frac{Pt - Pp}{Pt}$$

where: Pt is the percentage of porosity in an unloaded sample, and Pp is the percentage of porosity in a loaded sample sintered for the same length of time. Thus, a given load produces a constant proportional increase in densification, independent of time.

This suggests that loading, with low loads at least, does not introduce any new mechanism into the sintering process and that the applied force is merely added to the forces (surface tension) normally present in sintering. This interpretation is fortified by the absence of any change in the shape of the pores, as a result of loading, and by the finding of radial shrinkage in samples in which the sintering rate has been accelerated materially by axial loading.

If this conclusion is justified, it becomes apparent that there is a marked similarity between sintering and creep processes, wherein gradual deformation is induced by moderate loading. It is awkward, because of the different geometrical factors involved, to compare sintering rates with creep rates, as a test of their similarity, but it is feasible to compare the two processes in another way. It is well established that the load required to produce a given deformation in steady state creep is a linear function of the logarithm of time. A similar relationship can be demonstrated for sintering, see Graph B, Fig. 2, if

Table III—Density of Loose Powder Sintered under Load*

Load, Psi	Time, Hr	Density	Ideal Density, Pct
0	0	2.47	27.5
0	70	7.93	88.5
0	106	8.31	92.7
10	3	6.93	77.3
115	120	8.81	98.3

* All sintered at 1000°C in hydrogen.

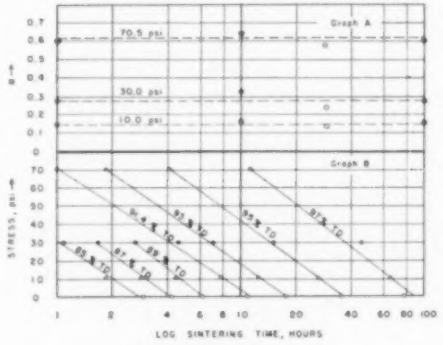

Fig. 2—Densification curves.

the load required to cause densification to progress to a given value is plotted as a function of the logarithm of time. Straight line plots appear justified by the data, and it is to be noted, further, that the point for zero load (ordinary sintering) generally falls upon the line.

In considering these results it should be remembered that the range of loads tested is not large. Were much higher loads used it is to be expected that different results would be obtained, because the creep process itself changes at higher loads, steady state creep giving way to a meeting of the initial and final transient creep mechanisms. At extremely low loads, if it be imagined that the surface tension forces could be taken away, or neutralized, it should be expected again that the process would change, for there appears to be a lower limit to the force that will induce observable creep. It is suggested, therefore, that the plots of Graph B are probably the intermediate straight segments of S-curves which should terminate at infinite time at zero load and at some load lower than the extrapolated values of the present curves at zero time.

Relating sintering and creep in this way does not solve the problem of the mechanism of either process. It does suggest, however, that what is learned about the mechanism of one may be applied to the other, thereby increasing the store of knowledge that may be applied to each.

Observations on Cleavage and Polygonization Of Molybdenum Single Crystals

by

Neng-Kuan Chen

and

Robert Maddin

THE {001} planes have been reported as the cleavage planes in body-centered cubic metals such as alpha-iron and tungsten.[1] However, in molybdenum, which is also body-centered cubic, experimental X-ray evidence indicating a similar cleavage plane still seems lacking. Tsien and Chow[2] observed microscopically in the extension at around 1000°C of molybdenum single crystalline wires 0.25 mm in diam that the fracture plane seemed to be parallel to the operative slip plane, which appeared to be {110} at that temperature. Zapffe[3] pointed out from fractographic study of polycrystalline molybdenum that "although the transgranular pattern is characteristically non-crystallographic, patterns occasionally reveal {100} cleavage." This has been generally assumed to be the case at ordinary temperatures.

In the present experiments, a single crystal of Fansteel molybdenum, ⅛ in. diam x 2 in. long, prepared by the methods described by Chen, Maddin, and Pond[4] was fractured at room temperature by bending. The fracture surface appeared to be quite similar to the cleavage surface of zinc and was crystallographic. A back-reflection Laue photogram was made using 35 kv copper white radiation; the X-ray

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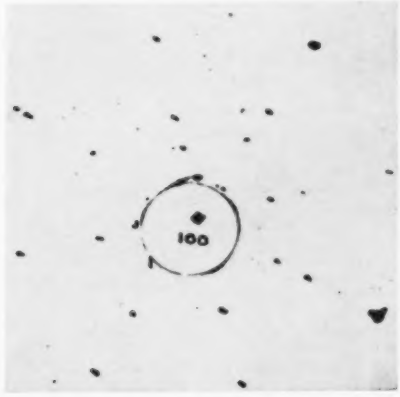


Fig. 1—Laue back-reflection photogram. X-ray beam perpendicular to (100) cleavage face of a molybdenum single crystal.

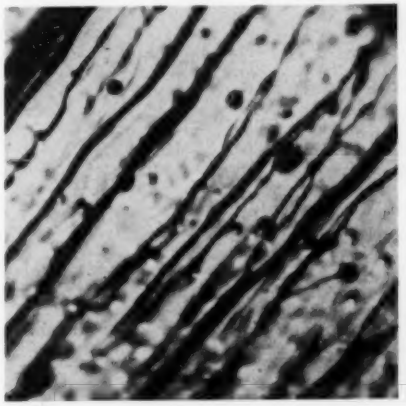


Fig. 2—Slip lines in a molybdenum single crystal at about 2400°C. X800.

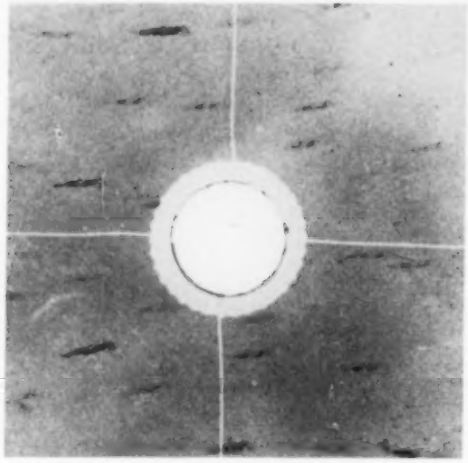
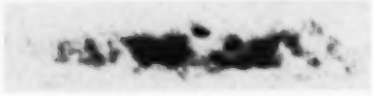


Fig. 3 (left)—Laue back-reflection photogram of a single crystal of molybdenum bent at about 2400°C.

Fig. 4 (below)—Enlargement of a Laue streak shown in Fig. 3. Streak is 4½° long.



beam was perpendicular to the cleavage surface. From Fig. 1 it can be concluded that the (100) plane is the plane of cleavage.

An interesting phenomenon apart from the cleavage described above was the polygonization of a single crystal of molybdenum after being bent at around 2400°C. The specimen was ⅛ in. in diam x 6 in. long containing a single crystal in the center section about 1¼ in. long. It was polished electrolytically and then reheated in the modified Andrade furnace[4] to a temperature of about 2400°C in 30 min. The specimen expanded freely up to a temperature of about 2200°C as measured by a dilatometer. At a temperature of between 2300° and 2400°C, the expansion was inhibited in some manner so as to cause a sudden sharp dip in the dilatometer reading. After examination at room temperature, a sharp bend through an angle of 15° was noted in the single crystal.

Slip lines observed at room temperature were broad and well-marked and appeared to be very branched, Fig. 2. X-ray photograms taken on three sides of the bent section revealed the orientation of the original crystal. However, the Laue spots were elongated and divided into small individual areas as shown in Figs. 3 and 4. The break-up of Laue spots in deformed crystals after annealing has been observed in aluminum, sodium, zinc and silicon ferrite. It has been termed polygonization by Orowan and Cahn.[5] They reasoned that an elastically bent lattice could be transformed into strain-free polygons by annealing. Recent work by Dunn and Daniels[6] on silicon-iron crystals also confirmed this phenomenon. Thus the present observation on the polygonization of a bent single crystal of molybdenum at high temperature is comparable to the behavior of other metals.

A stereographic plot of the Laue streaks in Fig. 3 is shown in Fig. 5. It should be noted that the rotation of the crystallites is about a [112] axis, which is in the slip plane (110) and 90° from the slip direction [111]. This checks with the microscopic observations of slip and also confirms the general type of crystal rotation in the plastic deformation of single crystals.

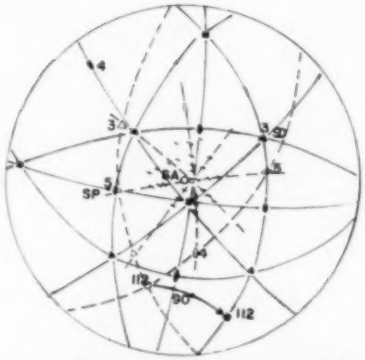


Fig. 5—Stereographic projection of Laue streaks (Fig. 3) showing crystal rotation.

Open representations show the beam perpendicular to the plot at center and stress axis coincides with horizontal diameter. Closed representations show X-ray beam and stress axis perpendicular to plot at center. *SD*, *SP*, and *SA* refer to slip direction, slip plane, and stress axis, respectively.

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Secondary Recrystallization in Copper Wire

by Guido Bassi

IT is known[1-3] that secondary recrystallization occurs in copper sheet with at least 90 pct reduction after annealing at high temperatures, 700° to 1000°C. Turkalo and Turnbull[4] have found recently that secondary recrystallization might occur even after annealing at such low temperatures as 500°C for a high purity, coarse-grained copper sheet. It will be shown in the following that in an electrolytic tough pitch copper wire, with a high degree of deformation, secondary recrystallization might occur at even lower temperatures.

A hot-rolled rod of 9.5 mm diam (temperature at which rolling commenced was 850°C) was drawn in continuous drawing machines to 0.4 mm, corresponding to a cross-section reduction of 99.8 pct. The texture in the center of the wire (the sample for X-ray analysis was etched to 0.15 mm diam) is a mixture of the [111] and the [100] direction, as can be seen from Fig. 1. This is in accordance with the result of Schmid and Wassermann.[5] After a few minutes annealing of the wire at 200°C, there is a noticeable recrystallization of the structure with a preferred orientation in the [100] direction at the expense of the [111] deformation texture, as Figs. 2 and 3 show. Farnham and O'Neill[6] reported a similar result. The final recrystallized structure shows mainly the [100] orientation. There is however a small amount of [111] and random orientations.

If the wire is annealed at 400°C, the recrystallized structure first shows a [100] texture, Fig. 4, but as the annealing time is increased the fine-grained structure transforms into coarse grains, Fig. 5, giving a new preferred orientation, Fig. 6. The calculations show this to correspond to the [112] direction. Even if the annealing that gives the primary recrystallization is carried out for six weeks at 200°C, the same secondary recrystallization texture is obtained if the annealing is continued at 400°C. Schmid and Wassermann[7] found the [112] texture, but only after annealing at 1000°C or higher.

The appearance of a secondary recrystallized

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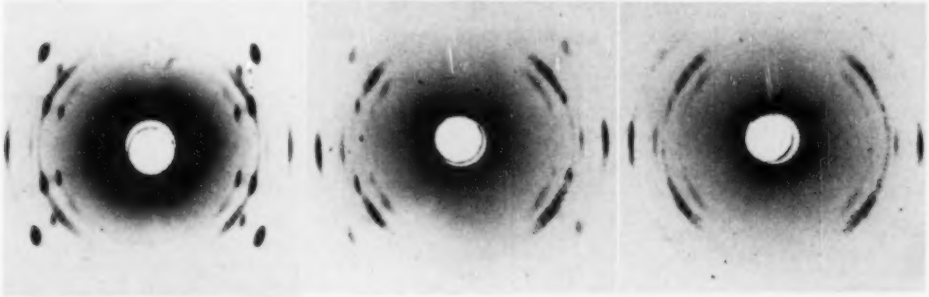

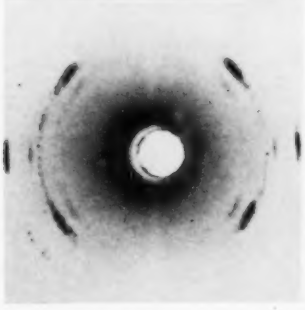

Fig. 1 (upper left)—Deformation texture of 0.4 mm wire showing [111] and [100] texture.
No rotation of specimen. Incident beam perpendicular to wire axis. Unfiltered copper radiation. Specimen etched to 0.15 mm.

Fig. 2 (center)—0.4 mm wire annealed 5 min at 200°C.
No rotation of specimen. Incident beam perpendicular to wire axis. Unfiltered copper radiation. Specimen etched to 0.15 mm.

Fig. 3 (right)—0.4 mm wire annealed 300 min at 200°C.
No rotation of specimen. Incident beam perpendicular to wire axis. Unfiltered copper radiation. Specimen etched to 0.15 mm.

Fig. 4 (lower left)—0.4 mm wire annealed 2 min at 400°C. X-ray diagram showing [100] texture.
Incident beam perpendicular to wire axis. Unfiltered copper radiation.

Fig. 5—0.4 mm wire annealed 30 min at 400°C. X200.

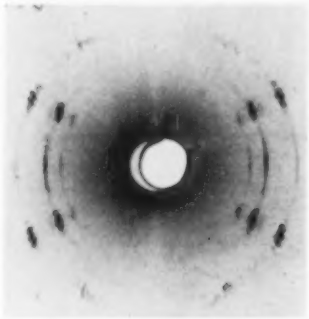

Fig. 6—0.4 mm wire annealed 30 min at 400°C showing [112] texture. Rotation of specimen. Incident beam perpendicular to wire axis. Unfiltered copper radiation. Specimen etched to 0.15 mm.

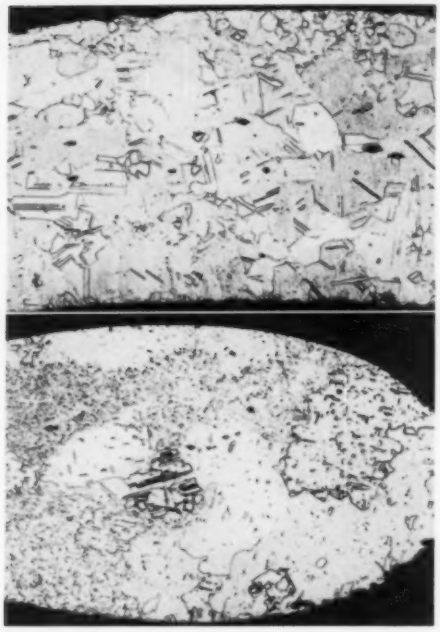

Fig. 7 (top)—9.5 mm hot-rolled rod annealed 1 hr at 1050°C, drawn to 0.4 mm, annealed 320 min at 400°C. X200.

Fig. 8 (bottom)—0.4 mm wire annealed 6 hr at 200°C, drawn to 0.38 mm, annealed 16 hr at 200°C. X200.

structure aligned in the [112] direction at such a low temperature as 400°C is due partly to the very high degree of deformation of the wire. The following two experiments show that the deformation is not the only factor of importance.

1—If electrolytic tough pitch copper is extruded at 925°C into a rod of 19 mm diam (average grain size, 0.05 mm) and drawn to 0.5 mm, corresponding to a reduction of 99.9 pct, then secondary recrystallization is found only after annealing at 800°C or higher. The interference spots on the X-ray film are not so sharp as in Fig. 6.

2—If the earlier mentioned hot-rolled rod of 9.5 mm is annealed 1 hr at 1050°C before being drawn to 0.4 mm, then the final recrystallized structure has a random orientation after annealing at 400°C. The grains are not too coarse, Fig. 7.

The deformation textures from these two experiments were similar to that of Fig. 1 and both showed a primary recrystallization structure with the [100] texture. The observations indicate that the occurrence of secondary recrystallization at 400°C, and the sharpness of the resulting texture are affected by other factors of the previous treatment, in addition to the final deformation. This may be the second last deformation and annealing. After the second last annealing there are areas or grains that are given a higher energy than the average in the last deformation. After the primary recrystallization these high energy grains have become grains with a lower energy than the average. As the annealing goes on, these grains grow at the expense of the neighboring grains with a higher energy. This theory regards secondary recrystallization merely as a coarsening of the primary recrystallized structure.

The [112] texture can be obtained at still lower temperatures. If the hard-drawn wire of 0.4 mm first is annealed 6 hr at 200°C, giving the [100] texture, and then drawn to 0.38 mm, corresponding to a reduction of 9.5 pct, secondary recrystallization with the [112] texture occurs even at 200°C, Fig. 8. Wilson and Kronberg[8] showed a similar result with coarse grains when giving a light reduction to a copper sheet with the cube texture. They regarded this not as secondary recrystallization but as primary recrystallization after critical deformation. It has not been found before however that primary recrystallization can occur after such a low reduction as 9.5 pct and annealing at 200°C. It seems more logical to call it secondary recrystallization.

Acknowledgment

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A Thermodynamic Study of the Reaction $CaS + H_2O = CaO + H_2S$ And the Desulphurization of Liquid Metals with Lime

by Terkel Rosenqvist

THE desulphurization of molten iron and steel is a very complicated process. One way to arrive at a better understanding of this process is to break it down into several simpler chemical processes that can be studied individually in the laboratory. For a study of the different factors that influence the equilibrium distribution of sulphur between liquid metals and slags, several simpler equilibria may be investigated. One very important subject is the determination of the escaping tendency of sulphur in the liquid metal and its dependency on temperature and composition of the melt. Several papers in this field have recently been published.[1, 2]

Another subject is the study of the sulphur capacity of the slag. A molten slag is indeed complex, and even if sulphur distribution data for a large variety of molten slags may give empirical data about their desulphurizing power, the importance of the individual components is still not quite clear. It is accepted generally that lime is the most important desulphurizing component in the slag. The present investigation has as its purpose to study the desulphurizing power of lime in its standard state, and to provide a basis for thermodynamic calculations of the desulphurizing power of various lime-containing slags.

The standard state of lime at steelmaking temperatures is solid calcium oxide, CaO. It can react with sulphur to form solid calcium sulphide, CaS. The relative stability of calcium oxide and calcium sulphide is expressed by the free energy of the reaction:

$$2CaO\ (s) + S_2\ (g) = 2CaS\ (s) + O_2\ (g)$$

The existing free energy data for this reaction, listed by Kelley[3] and Osborn,[4] are uncertain to about 10 kcal and are of limited value for a calculation of equilibrium constants.

Under the conditions prevailing in a melting furnace, the sulphur pressure may be expressed conveniently by the ratio H_2S/H_2 and the oxygen pressure by the ratio H_2O/H_2 (or CO_2/CO). The desulphurizing power of calcium oxide may, therefore, be studied by the reaction $CaO + H_2S = CaS + H_2O$.

A study of this reaction may be complicated by certain side reactions: Water vapor and hydrogen sulphide may react to form sulphur dioxide, and calcium sulphide may be oxidized to calcium sulphate. A thermodynamic calculation shows that these side reactions will be suppressed to insignificance if the equilibrium is studied in the presence of an excess of hydrogen.

The apparatus used is shown in Fig. 1. About 10 g calcium oxide and 20 g calcium sulphide (laboratory qualities) were intimately mixed, and some water was added to make a thick paste. The paste was put into a thimble of zirconium silicate, which was placed within the constant temperature zone of a furnace, and capillary refractory tubes were attached in both ends. After the mixture had been heated in dry hydrogen at 1000°C for several hours all $Ca(OH)_2$ and $CaCO_3$ had decomposed and $CaSO_4$ was reduced, so only CaO and CaS remained in the thimble forming a porous plug.

The mixture was examined by X-ray diffraction after the initial reduction in dry hydrogen as well as after the subsequent experimental runs up to 1425°C. It was shown that crystalline calcium oxide and calcium sulphide were always present together in about equal amounts. The unit cell edges were found to be 4.80A for CaO and 5.68A for CaS in good agreement with existing literature values.[5] This shows that the mutual solid solubility is very small, and that the compounds are present in their standard states.

Purified hydrogen was passed through water saturators kept at constant temperature in a thermostat bath. The amount of water vapor saturation was checked by means of a dew point method, not shown on Fig. 1. The gas mixture was passed through the capillary inlet into the furnace, where it was sifted through the porous plug of calcium oxide and calcium sulphide.

The hydrogen sulphide present in the outgoing gas was absorbed in a zinc acetate solution and the hydrogen was collected over water. When one liter of hydrogen had been collected, the amount of hydrogen sulphide was determined by iodometric titration. As one molecule of H_2O is used for the formation of each molecule of H_2S, the equilibrium ratio H_2S/H_2O would be $\frac{(H_2S)}{(H_2O)-(H_2S)}$, where (H_2O) is the molar concentration in the ingoing gas, and (H_2S) the molar concentration in the outgoing gas. In the present work (H_2S) was always very small compared to (H_2O).

In order for the observed H_2S/H_2O ratio to represent the true equilibrium ratio the gas flow has to be: 1—Sufficiently slow to give a complete establishment of equilibrium, and 2—sufficiently fast to counteract thermal diffusion. Incomplete reaction would give a value decreasing with increasing flow rate, and thermal diffusion would give a value increasing with decreasing flow rate. When inlet and outlet tubes of about 2 sq mm cross-section were used, the observed gas ratio was independent of the flow rate between 15 and 125 cc per min, Fig. 2. In this range, therefore, the observed gas ratio represents true equilibrium.* For the rest of the in-

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* This was not found to be true when the inlet and outlet tubes were of about 20 sq mm cross-section. In that case thermal diffusion was significant at a flow rate of 125 cc per min.

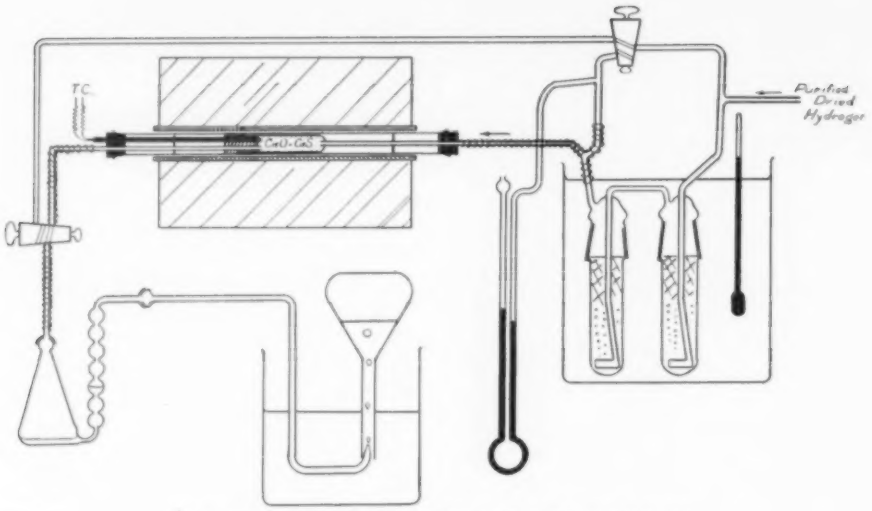

Fig. 1—Apparatus for study of the equilibrium $CaS + H_2O = CaO + H_2S$.

vestigation the flow rate was kept between 50 and 80 cc per min.

Fig. 3 shows that when the H_2O/H_2 ratio was varied over a wide range the H_2S/H_2 ratio varied proportionally. This shows that the hydrogen sulphide in the outgoing gas actually is formed by the proposed reaction.

A thermocouple was inserted in the reaction mixture and the measurements were made from 750° to 1425°C. At the highest temperature a slight slagging was observed on the contact between the thermocouple and the reaction mixture, but without affecting the bulk of the mixture.

Experimental Results

The experimental results listed in Table 1 represent the average of from two to five single analyses for each temperature. In Fig. 4 the logarithm of the gas ratio is plotted vs. $1/T$.

For the reaction $CaS(s) + H_2O(g) = CaO(s) + H_2S(g)$, the enthalpy is:

$$\Delta H = 15{,}650 \text{ cal}$$

and Gibbs free energy:

$$\Delta F^\circ = 15{,}650 - 0.87 \cdot T \text{ cal}$$

These values apply to temperatures between 750° and 1425°C, but as ΔCp of the reaction is small, they are assumed valid up to steelmaking temperatures of about 1600°C.

In this temperature range the free energy is about 3 kcal higher than that calculated from Osborn's free energy survey.[4]

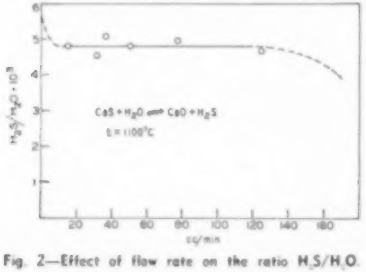

Fig. 2—Effect of flow rate on the ratio H_2S/H_2O.

The dotted lines indicate the expected effects of thermal diffusion at low flow rates, and incomplete reaction at high flow rates.

Desulphurization of Liquid Copper

The escaping tendency of sulphur dissolved in a molten metal may be expressed conveniently by the equilibrium H_2S/H_2 ratio which can be determined from the reaction: $S(\text{dissolved}) + H_2 = H_2S$. If this reaction is combined with the reaction $CaO + H_2S = CaS + H_2O$, one obtains:

$$S(\text{dissolved}) + CaO + H_2 = CaS + H_2O$$

As for low concentrations, the sulphur activity is closely proportional to the sulphur concentration, the sulphur content of a melt in equilibrium with solid calcium oxide and solid calcium sulphide will be closely proportional to the ratio H_2O/H_2 in the atmosphere.

In order to see if this relationship actually holds, the desulphurization of liquid copper with lime was investigated. It was hoped in that way to obtain

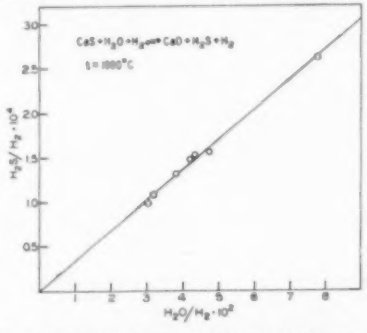

Fig. 3—Correlation between H_2O/H_2 and H_2S/H_2 ratio.

some information that might be useful for an understanding of the factors affecting the desulphurization of iron and steel. The principles behind the reaction would be the same for copper as for iron.

Hydrogen, saturated with water vapor at various temperatures, was bubbled through a copper melt in contact with solid CaO and solid CaS until equilibrium between the gas, the liquid, and the solid phases was established, Fig. 5. All runs were made at 1200°C. Most of the runs were carried out with about 50 g copper of 1.5 to 2.5 pct initial sulphur content and 3 to 5 g calcium oxide. Calcium sulphide then was formed during the reaction. A few preliminary runs, No. 12 and No. 16 (Table II), were made with a smaller amount of pure copper in contact with a larger amount of CaO and CaS. These runs gave results in agreement with the rest of the work. In all cases crucibles of zirconium silicate were used.

The amount of oxygen introduced in the copper melt by this procedure can be calculated from the recent investigation by Girardi and Siebert.[6] At 1200°C the oxygen concentration expressed in weight percentage will about equal $H_2O/H_2 \cdot 10^{-4}$. As in the present work the ratio H_2O/H_2 was maintained between 1/20 and 1/2, the oxygen content will be of the order of 10^{-5} pct. It is assumed that this will have no significant effect on the activity coefficient of sulphur in the melt.

Samples were drawn from the liquid copper by means of an arrangement similar to that used by Hatch and Chipman.[7] In order to prevent air from leaking into the apparatus when the sampler was inserted or removed, the tube was flushed with nitrogen during these operations, Fig. 5. The entire sample, 2 to 5 g, was dissolved in nitric acid and bromine and, after removal of the copper by electrolysis, sulphur was determined by precipitation as $BaSO_4$.

In some cases X-ray diffraction diagrams were taken of the crust of solids that remained in the crucible after the copper had been poured out. Invariably the lines of CaO and CaS were found proving that these compounds were present in their standard state.

In Fig. 6 the approach to equilibrium is studied as a function of time for a sequence of different gas compositions. Even if the scattering of the points is large, it is evident that there is no systematic trend with time after 5 hr of constant gas composition. Furthermore, Fig. 6 shows that the sulphur content is established equally well from the high as from the low side. It is therefore concluded that equilibrium values are established in about 5 hr, and in Table II are listed the results of various runs based on samples drawn after 5 to 29 hr of constant gas composition. The values were obtained about equally by approach from the high as from the low side.

During the reaction a small amount of hydrogen sulphide is formed, corresponding to the equilibrium H_2S/H_2 ratio. This causes a removal of sulphur from the copper melt, a loss which has to be replenished by transfer of sulphur from the "slag." Equilibrium can only be expected when a significant amount of CaS remains, and when the rate of transfer between the slag and the metal is higher than the rate at which sulphur is removed as hydrogen sulphide. The general agreement between the values obtained by approach from both sides indicates that this is the case. Furthermore, the rate of sulphur removal

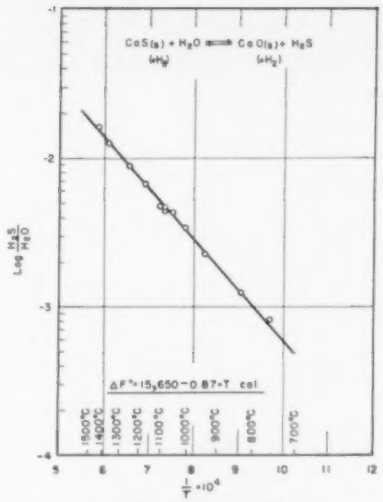

Fig. 4—Log H_2S/H_2O against 1/T.

can be estimated from the H_2S/H_2 ratio and the gas flow and, in the present case, is between 0.002 and 0.02 g per hr. This appears to be considerably less than the rate of sulphur transfer between the copper melt and the "slag" as estimated from the rate at which equilibrium is approached, Fig. 6.

Nevertheless, a certain instability is introduced due to the continuous removal of sulphur as hydrogen sulphide. This instability may be one of the reasons for the scattering of points in Figs. 6 and 7.

Fig. 7 shows that for less than 1 pct S the sulphur content of the copper melt is closely proportional to the ratio H_2O/H_2. The scale on the right hand side of Fig. 7 gives the corresponding H_2S/H_2 ratio calculated from the data given in Table I.

The equilibrium S(in Cu) + H_2 = H_2S was investigated recently by Sudo.[8] For a temperature of 1200°C his data give an equilibrium ratio

$$\frac{H_2S}{H_2 \cdot \%S}$$

equal to about $4.5 \cdot 10^{-4}$, valid for sulphur contents up to 0.87 pct. As seen from Fig. 7 this value is in very good agreement with the results of the present investigation.

For molten copper in equilibrium with molten cuprous sulphide Schuhmann and Moles[9] have found the H_2S/H_2 ratio equal to $4.2 \cdot 10^{-3}$ at 1200°C. According to Fig. 7 this should correspond to a maximum solubility of about 1 pct S in liquid copper. This is about half the solubility that is generally

Table I. Experimental Results

Analysis Number	Temperature, °C	H_2O/H_2 10^3	H_2S/H_2 10^4	H_2S/H_2O 10^3
44-49	1103	4.39	2.11	0.481
53-55	1251	4.58	4.06	0.887
56-57	940	7.42	1.73	0.233
58-59	1081	7.36	3.50	0.475
60-61	1081	4.53	2.00	0.442
62-63	1067	4.38	1.91	0.436
64-66	758	9.01	0.74	0.082
67-68	832	8.66	1.07	0.124
69-70	1002	4.63	1.59	0.343
71-72	1176	4.63	3.10	0.670
73-75	1350	4.67	6.15	1.317
76-77	1425	5.34	8.87	1.66

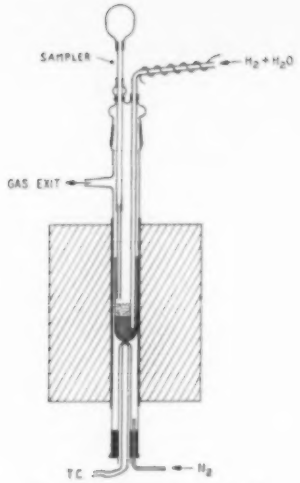

Fig. 5—Apparatus for study of copper desulphurization.

accepted.[16] In order to verify this finding, extended work by this and other methods have to be made.

Application to Blast Furnace Desulphurization

In a recent careful study, Hatch and Chipman[7] determined equilibrium values for the distribution of sulphur between carbon-saturated iron and various blast furnace slags in an atmosphere of pure CO. These authors were unable, however, to correlate their results with any theoretically calculated distribution coefficient. This may be due partly to insufficient knowledge about the activities of various constituents in the slag.

In this section Hatch and Chipman's data will be used, in connection with the data obtained in the present investigation, to calculate activity data for the slag.

If the reaction $CaS + H_2O = CaO + H_2S$ is combined with the water gas reaction $H_2O + C = H_2 + CO$ to give:

Table II. Desulphurization of Molten Copper

Sample Number	H_2O/H_2	Wt Pct S	Sample Number	H_2O/H_2	Wt Pct S
12	0.418	0.65	50	0.078	0.16
			51	0.079	0.14
16	0.192	0.33			
			56	0.184	0.26
21	0.256	0.33	57	0.184	0.27
22	0.257	0.32			
			59	0.245	0.31
23	0.145	0.19			
24	0.146	0.18	63	0.038_5	0.07
25	0.148	0.31	64	0.038_5	0.08
26	0.080	0.12	65	0.043_7	0.09
27	0.080	0.13	66	0.043_8	0.08
28	0.079	0.13			
			68	0.058_3	0.08
29	0.187	0.29			
30	0.183	0.28			
31	0.185	0.22	76	0.512	1.0–
			77	0.527	0.95
33	0.138	0.18	82	0.340	0.57
36	0.138	0.22	84	0.348	0.48
37	0.059	0.09	87	0.253	0.30
			88	0.260	0.45

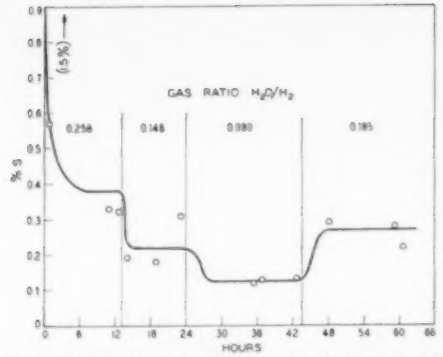

Fig. 6—Effect of time on the sulphur content of the copper melt.

The horizontal levels given for each gas composition correspond to the sulphur values given by the curve on Fig. 7.

$$CaO + H_2S + C = CaS + H_2 + CO$$

then

$$\Delta F^\circ = 17{,}210 - 34.09 \cdot T \text{ cal}$$

is obtained. The escaping tendency of sulphur in liquid iron is given by Sherman, Elvander, and Chipman:[1]

$$S \text{ (in Fe)} + H_2 = H_2S$$

$$\Delta F^\circ = 9{,}840 + 6.54 \cdot T \text{ cal}$$

The reference state for sulphur here is chosen to be an ideal 1 pct solution of sulphur in pure iron. For the reaction:

$$S \text{ (in Fe)} + CaO + C = CaS + CO$$

therefore is obtained:

$$\Delta F^\circ = 27{,}050 - 27.55 \cdot T \text{ cal}$$

or at a temperature of 1500°C:

$$K = \frac{a_{CaS} \cdot p_{CO}}{a_{CaO}[S] \cdot f_s \cdot a_C} = 490$$

Under the conditions studied by Hatch and Chipman p_{CO} and a_C were both unity. For iron saturated with carbon at 1500°C, Morris and Buehl[2] found the activity coefficient f_s equal to about 5.8.

This gives for a system in equilibrium with graphite and a CO atmosphere:

$$\frac{a_{CaS}}{a_{CaO}} = 2842.\,[S]$$

The activities a_{CaS} and a_{CaO} are referred to the pure solids as standard state, and [S] is the sulphur content of the iron melt in weight percentage.

The activity of calcium oxide in a calcium silicate melt can be approximately derived from the free energy diagram of the system $CaO\text{-}SiO_2$ given by Darken.[11] For a melt with the ratio $CaO/SiO_2 = 1$, $a_{CaO} \approx 0.010$ and for a melt with $CaO/SiO_2 = 1.5$, $a_{CaO} \approx 0.025$. In Table III these values are combined with sulphur distribution data obtained by Hatch and Chipman and values for a_{CaS} are calculated.

In Fig. 8 the activity of CaS is plotted vs. the sulphur content of the slag, (S). For both types of slag the activity may be represented adequately by one single curve. The activity seems to reach unity at about 10 pct S. This value agrees rather well with McCaffery and Oesterle's[17] experimental values

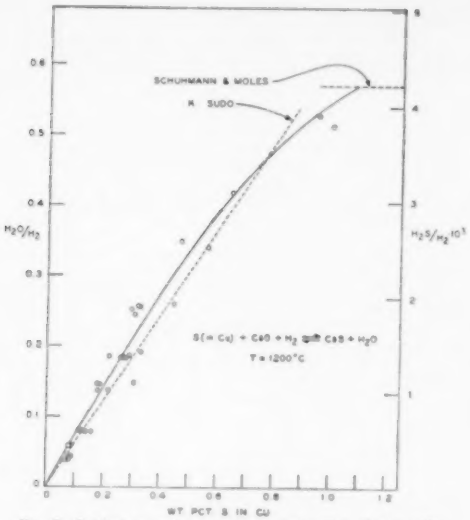

Fig. 7—Sulphur in molten copper as a function of the ratio H_2O/H_2.

The right hand scale gives the corresponding H_2S/H_2 values.

for the solubility of CaS in various blast furnace slags. These authors found the CaS solubility at 1500°C to vary from about 8 pct S for acid slags to about 11 pct for the more basic slags. Glaser[12] found the solubility of CaS in a pure $CaSiO_3$ melt corresponding to 5.5 pct S at 1500°C. Furthermore Glaser showed that at a somewhat higher sulphur content and temperature a region of liquid immiscibility occurred. This means that a_{CaS} would be expected to show a pronounced positive deviation from ideality. This is confirmed by Fig. 8.

The agreement between the activity data given in Fig. 8 and the activities to be expected from solubility data actually confirms the values for a_{CaO} which with considerable uncertainty were derived from Darken's free energy diagram.

If the slag had contained an excess of solid CaS, a_{CaS} would be unity and at 1500°C:

$$a_{CaO} = \frac{3.52}{[S]} \cdot 10^{-4}$$

An experimental determination of the sulphur content of the iron melt under these conditions may give us a possible way to determine activity values for CaO in slags of various compositions and basicities.

The general conclusion of this investigation is that the activity of sulphur in a molten metal in equilibrium with a slag will be proportional to the atomic oxygen fugacity in the system, expressed by

Table III. Activities in Calcium Silicate Slags

$CaO/SiO_2 = 1$, $a_{CaO} = 0.010$				$CaO/SiO_2 = 1.5$, $a_{CaO} = 0.025$			
(S) pct	$\frac{(S)}{[S]}$	$\frac{a_{CaS}}{a_{CaO}}$	a_{CaS}	(S) pct	$\frac{(S)}{[S]}$	$\frac{a_{CaS}}{a_{CaO}}$	a_{CaS}
1.5	107	39.8	0.398	1.5	250	17.1	0.426
2.5	140	51.2	0.512	2.5	335	21.3	0.533
5.0	180	79.6	0.796	5.0	440	32.4	0.810

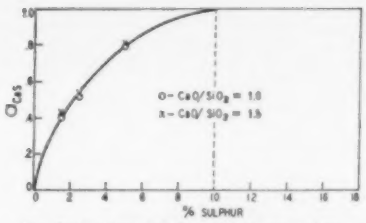

Fig. 8—Activity of CaS in blast furnace slags.

the ratio H_2O/H_2, CO_2/CO, or CO/a_C, and proportional to the ratio a_{CaS}/a_{CaO} in the slag. The activities a_{CaO} and a_{CaS} are exactly defined quantities and do not correspond to any assumed picture of "free lime" or "sulphur combined with calcium."

Most probably liquid slags are highly ionized and, for the lack of any dissociation constants, activities can be defined for the sulphur and oxygen ions, so that:

$$\frac{a_{CaS}}{a_{CaO}} = \frac{a_{S^{2-}}}{a_{O^{2-}}}$$

If the ratio between the activity $a_{S^{2-}}$ and percentage of sulphur in the slag (S) is called $\gamma_{S^{2-}}$, it will be seen that the amount of sulphur a given slag will absorb under a given oxygen and sulphur fugacity will be proportional to $a_{O^{2-}}/\gamma_{S^{2-}}$.

This quantity can be called the sulphur-capacity of the slag. It is a fundamental, intrinsic property of the slag, the detailed knowledge of which would be of considerable importance. This quantity may be determined experimentally by passing a controlled mixture of hydrogen, hydrogen sulphide, and water vapor through the molten slag and determining the equilibrium sulphur content (S). The relation then will be:

$$\frac{a_{O^{2-}}}{\gamma_{S^{2-}}} = K \cdot \frac{H_2O}{H_2S} (S)$$

K is equal to the equilibrium constant for the reaction $CaS + H_2O = CaO + H_2S$, as given in Table I and Fig. 4.

A research program along these lines is planned.

Summary

The desulphurizing power of calcium oxide in its standard state has been investigated.

1—The reaction CaS (s) + H_2O (g) = CaO (s) + H_2S (g) has been studied from 750° to 1425°C. The Gibbs free energy of the reaction can be expressed as follows:

$$\Delta F^\circ = 15{,}650 - 0.87 \cdot T.$$

See Table I and Fig. 4.

2—The desulphurization of liquid copper with calcium oxide has been studied at 1200°C. It is found that the sulphur content in the copper is closely proportional to the H_2O/H_2 ratio in the atmosphere, as would be expected in accordance with the equation:

$$S\ (\text{in Cu}) + CaO(s) + H_2(g) = CaS(s) + H_2O(g)$$

The results indicate a maximum solubility of sulphur in liquid copper at 1200°C of about 1 wt pct, Table II and Fig. 7.

3—The obtained data for the desulphurizing power of calcium oxide have been combined with blast furnace desulphurization data, obtained by

Hatch and Chipman,[7] and with calcium oxide activity data obtained from Darken's free energy diagram of the system CaO-SiO_2.[11] Values for a_{CaS} are calculated for slags of various basicities and sulphur contents, Table III and Fig. 8.

With emphasis on the ionic theory for liquid slags the expression $\frac{a_{CaO} \cdot S}{a_{CaS}} = \frac{a_{O^{2-}}}{\gamma_{S^{2-}}}$ is suggested as a measure for the sulphur capacity of the slag.

Acknowledgments

The first part of this work was carried out with the help and assistance of E. M. Cox, the second part with assistance of B. L. Dunicz. Their help is thankfully acknowledged. The copper-sulphur samples were analyzed by Miss M. C. Bachelder, Mrs. E. W. Nobile and A. A. Roman; thanks are due to them.

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Technical Note

Effect of Hardness on Temper Brittleness

by D. C. Buffum and L. D. Jaffe

QUANTITATIVE measurements of the temper brittleness of steel are made by comparing the difference between embrittled and unembrittled specimens in the temperature of transition from ductile to brittle fracture. Since hardness affects the transition temperature, a study of the combined effects of hardness and temper brittleness appeared desirable.

In this investigation a commercial SAE 3140 steel, which has been reported on previously in temper brittleness studies,* was used. Blanks from this steel were austenitized for 1 hr at 900°C and water quenched. The blanks were then divided into six groups and further heat treated as follows: Group 1—tempered at 675°C for 4 hr and water quenched; Groups 2, 3, 4, and 5—tempered at 675°, 650°, 625°, and 600°C respectively for 1 hr and water quenched; and Group 6—tempered at 500°C for ½ hr and water quenched.

Each of these groups was divided into two parts; one part was tested without further heat treatment, and the other was embrittled for 48 hr at 500°C and water quenched. Tempering treatments between 500° and 600°C were avoided because of the rapid embrittlement occurring in that range for this steel.

The heat-treated blanks were machined into standard V-notched Charpy bars. Each group was tested over a range of temperatures on a 217 ft-lb Charpy machine.

The energies necessary to fracture the bars and the percentage fibrous fracture of each bar were recorded. The transition temperatures were obtained from a plot of the percentage fibrous fracture as a function of testing temperature. They were taken as the lowest point on these curves at which the fracture was 100 pct fibrous. The transition temperatures for both embrittled and unembrittled specimens are presented in Fig. 1 as function of the hardness. It will be noticed in this figure that the point for the unembrittled condition at 21 Rockwell C is out of line. These specimens were tempered for 4 hr at 675°C and this point indicated that under isothermal conditions at this temperature, as is well known, embrittlement may develop fast enough to more than offset the effects of softening.

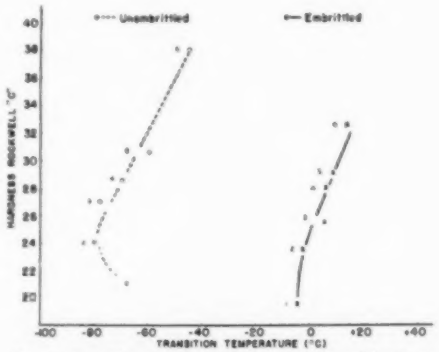

Fig. 1—Transition temperature as a function of hardness. Numbers indicate heat treatment groups.

From this data, it was concluded that the difference between transition temperatures for the embrittled and unembrittled conditions at any given hardness, within the range of Rockwell C 24½ to 32½, is constant.

It is also concluded that, within the hardness range studied, the transition temperatures for embrittled and unembrittled specimens rise in a parallel fashion with an increase in hardness.

The authors wish to acknowledge the assistance of Frank Carr in this work.

D. C. BUFFUM, Junior Member, and L. D. JAFFE, Member AIME, are associated with the Watertown Arsenal, Watertown, Mass.

TN 82E. Manuscript, April 23, 1951.

* L. D. Jaffe and D. C. Buffum: Isothermal Temper Embrittlement. *Trans.* ASM (1950).

Discussion — Institute of Metals Division*

Chicago Meeting, October 1950

An Experimental Survey of Deformation and Annealing Processes in Zinc (paper by D. C. Jillson. JOURNAL OF METALS, August 1950, p. 1009) 541

A Study of the Plastic Behavior of High-Purity Aluminum Single Crystals at Various Temperatures (paper by F. D. Rosi and C. H. Mathewson. JOURNAL OF METALS, September 1950, p. 1159) 545

A Study of Strain Markings in Aluminum (paper by Bani R. Banerjee. JOURNAL OF METALS, September 1950, p. 1126) 547

Activation Energy for Recrystallization in Rolled Copper (paper by B. F. Decker and D. Harker. JOURNAL OF METALS, June 1950, p. 887) 548

Recrystallization Reaction Kinetics and Texture Studies of a 50 Iron 50 Nickel Alloy (paper by William E. Seymour and David Harker. JOURNAL OF METALS, August 1950, p. 1001) 549

The Textures of Cold-Rolled and Annealed Titanium (paper by Howard T. Clark, Jr. JOURNAL OF METALS, September 1950, p. 1154) 549

Production and Examination of Zinc Single Crystals (paper by D. C. Jillson. JOURNAL OF METALS, August 1950, p. 1005) 550

The Structure of Intermediate Phases in Alloys of Titanium with Iron, Cobalt, and Nickel (paper by Pol Duwez and Jack L. Taylor. JOURNAL OF METALS, September 1950, p. 1173) 551

On the Martensitic Transformation at Temperatures Approaching Absolute Zero (paper by S. A. Kulin and Morris Cohen. JOURNAL OF METALS, September 1950, p. 1139) 551

The Isothermal Transformation of a Eutectoid Beryllium Bronze (paper by Ronald H. Fillnow and David J. Mack. JOURNAL OF METALS, October 1950, p. 1229) 553

The Effect of Alloying Elements on the Plastic Properties of Aluminum Alloys (paper by J. E. Dorn, P. Pietrokowsky and T. E. Tietz. JOURNAL OF METALS, July 1950, p. 933) 556

The Properties of Some Magnesium-Lithium Alloys Containing Aluminum and Zinc (paper by Robert S. Busk, Donald L. Leman, and John J. Casey. JOURNAL OF METALS, July 1950, p. 945) 556

The Effect of Sodium Contamination on Magnesium-Lithium Base Alloys (paper by P. D. Frost, J. H. Jackson, A. C. Loonam, and C. H. Lorig. JOURNAL OF METALS, September 1950, p. 1171) 557

Hydrogen Embrittlement of SAE 1020 Steel (paper by J. B. Seabrook, N. J. Grant, and Dennis Carney. JOURNAL OF METALS, November 1950, p. 1317) 558

Aging Characteristics of Magnesium-Lithium Base Alloys (paper by P. D. Frost, J. G. Kura, and L. W. Eastwood. JOURNAL OF METALS, October 1950, p. 1277) 560

Hydrogen Solubility in Aluminum and Some Aluminum Alloys (paper by W. R. Opie and N. J. Grant. JOURNAL OF METALS, October 1950, p. 1237) 561

Dendritic Crystallization of Alloys (paper by B. H. Alexander and F. N. Rhines. JOURNAL OF METALS, October 1950, p. 1267) 561

* TP 2090E

An Experimental Survey of Deformation and Annealing Processes in Zinc

by D. C. Jillson

DISCUSSION, B. Averbach presiding

J. R. Lane *(Metals Research Laboratory, Washington)*—A new type of deformation called "kinking" has recently been described. Is there any relation between the "rumpling" described in this paper and "kinking?"

D. C. Jillson (author's reply)—Both are manifestations of bending about [210] axis. The difference is one of degree.

W. C. Ellis *(Bell Telephone Laboratories, New York)*—Some observations of deformation in zinc recorded in this paper may be applicable generally to flow in metals. One of these, deformation in torsion without evidence of slip or twinning in the early stages and with startling ease, when the twist is about the hexagonal axis, adds another method of flow to the presently increasing list of mechanisms. This illustrates again that a crystal will utilize any realizable process to flow and relieve stress. The process is not necessarily classical directional slip—in this case, it is rotational slip. The question naturally occurs: Will face-centered cubic metals stressed by twisting about an octahedral axis flow in a similar manner by rotation on an octahedral plane? I would like to ask Dr. Jillson if he has made any experiments or knows of any experiments of this type on face-centered cubic metals? Face-centered cubic metals possibly would behave differently from zinc, since, for one thing, the stacking sequence is different for the two structures. The results of such experiments, however, would be instructive in providing more information about deformation processes.

D. C. Jillson—Dr. Roy E. Swift, working in the Hammond Laboratory at Yale, performed a twist test on a single crystal of brass. The work has not been published, and I do not know the crystallographic direction of the axis of the specimen used.

Lo-ching Chang *(Columbia University, New York)*—Observations similar to Figs. 1 and 2 of the paper were obtained by us during the bending and unbending of an orthorhombic Au-Cd alloy.[81] This orthorhombic alloy is the product of diffusionless transformation from a single crystal of β Au-Cd alloy (CsCl structure) containing 47.5 atomic pct Cd on cooling to about 60°C.[82] Referring to the effects of annealing, has the author tried any long time high temperature anneal, such as 150 to 200 hr at 400°C?

D. C. Jillson—No.

C. Crussard *(Ecole des Mines, Paris, France)*—I

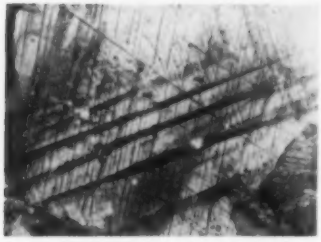

Fig. 16—Grain at the surface of a uranium polycrystal compressed 2 pct, showing twinning, slip, and kink bands. The kink bands are the broad markings. X100.
Area reduced approximately 66 pct for reproduction.

would like to mention a few observations on the twinning and detwinning of a zinc crystal, which I made[16] and which are in agreement on many points with those of Dr. Jillson. The crystal was made by recrystallization, which is rather easy with impure zinc, but becomes more difficult, the purer the metal; as I have explained elsewhere,[16] with the 99.99 pct Zn used, it was very difficult to prepare single crystals by this method; only three were obtained.

One crystal had an orientation with the basal plane parallel to the axis of the specimen. This made it unsuitable for elongation; but it could easily twin by torsion. The twin was studied by torsion under the microscope. As observed by Dr. Jillson, a rather strong torque had to be applied to make the twin start, with a click; after which, the twin grew under a very small torque, without hardening. Reversal of the stress caused progressive detwinning, under a small torque, until a faint line only was visible. But this last trace did not disappear; under a new reversal of stress it could grow again under a small torque, as the first time. The operation could be repeated.

When a fine line was left, it could disappear (with a click) under a strong (reverse) torque, of the same order as that necessary to initiate the twin. After complete disappearance of the twin, when I tried to produce a new twin, it started in another place. Thus it seems that the "nucleus" of a twin is hard to produce; but once produced, it has an appreciable stability.

The "rumpling" shown by the author is very interesting. It can be interpreted as a polygonization during deformation. The latter has been observed in my laboratory[16] in all types of deformation in aluminum; it is very strongly developed during creep. In other words, dislocations show two competitive trends: To cluster in walls, or to trigger "avalanches," if they have enough kinetic energy. The latter factor is the key to the whole problem.

D. C. Jillson—It is difficult to grow strain-anneal single crystals of high-purity zinc, as reported by Mathewson and Phillips.[16] We found at that time that a critical content and, perhaps, dispersion of iron was helpful.

Regarding detwinning, it seems likely that the conditions in Professor Crussard's torsion specimen were not so simple as those in some of our specimens and that his inability to detwin them completely without an increase in stress may have been due to this. We were frequently unable to detwin completely in specimens where the deformation was more extensive.

R. W. Cahn (*Ministry of Supply, Atomic Energy Research Establishment, Harwell, Berks, England*)—Dr. Jillson's observations on the widespread prevalence of glide-plane bending in zinc will, I am sure, assist considerably towards a complete understanding of the plastic behavior of metals. What is particularly interesting is the apparently general tendency for uniform curvature in a lattice to turn into a segmented or "polygonized" curvature. This is brought out by the X-ray photographs in the paper which show that a segmented curvature exists in a zinc crystal immediately after bending, albeit on a very fine scale. This observation is also in line with Ramsey's observations[16] on the cell structure of polycrystalline zinc extended at room temperature. I have found what is almost certainly an instance of the same phenomenon both in stretched and in compressed polycrystalline uranium, Fig. 16. Here there are pairs of bend planes, of opposite sense, approximately normal to the slip direction, just as in the cases illustrated by Jillson: These pairs constitute "kink bands."

It seems to me that in all these cases, the basic phenomenon is that of the single bend plane. A kinked zinc crystal contains numerous such planes of both senses, combined with sharp continuous curvature, while a bent crystal, according to Dr. Jillson, contains a very large number of feeble bend planes of the same sense. The so-called deformation bands in aluminum, studied at Yale University, by Honeycombe,[17] and by myself among others, are probably constituted by pairs of bend planes, as recently suggested by Mathewson.[16] Fig. 17 is a photograph of such a band in aluminum. It was generally found, as here, that one side of the band was more sharply curved than the other. The occurrence of such bands formed in tension, and kink bands in zinc formed by compression, are not consistent with Dr. Jillson's picture suggested at the end of his paper. He proposes that bands are formed and disappear again periodically, each such cycle being associated with a sort of slip quantum. In the cases just cited, however, the bend planes, once created, form a permanent barrier in the lattice: They become progressively sharper, each acting as a sieve in retaining dislocations of one sign. The effect of annealing seems to be to sharpen the curvature. This may happen by a segmentation of an apparently continuous curvature, as in Fig. 18, which was made from a deformation band in an aluminum crystal annealed after extension, repolished after annealing, and then slightly stretched again; or it may happen by a coalescence of segments already existing, as would appear to be the case when a bent zinc crystal is annealed. The motion of dislocations involved in such processes can be very considerable and may be evidenced by a visible change in the shape of a specimen on annealing. Thus Fig. 19 is a photograph of the surface of an aluminum crystal which was stretched with the generation of deformation bands, repolished, and then annealed. The anneal brought about the change of structure also shown in Figs. 17 and 18, but here this change revealed itself by a marked rumpling on the previously smooth surface. (Figs. 17 and 18 are sections almost parallel to the slip direction, Fig. 19 a section inclined to this direction.) This rumpling distinguishes the process in question from grain boundary migration, which generally does not affect the specimen surface, except for minor effects attributed to thermal etching.

This suggests that dislocation models of grain

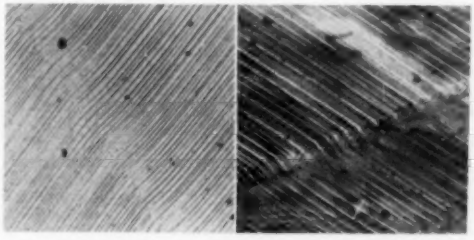

Fig. 17 (left)—Deformation or kink band in an aluminum crystal stretched 24 pct. X250.

Fig. 18 (right)—Aluminum crystal stretched 31 pct, annealed 1 hr at 450°C, repolished and slightly stretched. X260.
Areas reduced approximately 66 pct for reproduction.

boundaries should be re-examined, since on the basis of such a model boundary migration in a specimen should affect its shape, just as polygonization of a deformation band does. The motion of a plane array of dislocations normal to itself is in fact equivalent to a shear. Fig. 20 shows this in an exaggerated fashion, and also shows how such a shear would be expected to occur under the action of an applied shear stress. Experimental data on this point might be rather informative. Indirect evidence that applied stress accelerates the motion of dislocation arrays can be found in recent experiments on creep.[59, 60] It was found that during the creep of aluminum, the lattice became segmented into mutually inclined "cells." This process also occurs, in the way described above, if a specimen is stretched rapidly and then annealed without applied stress, but in the latter case the segmented structure develops more slowly.

The marked effect of applied stress on polygonization is brought out clearly by the following experiment. Two specimens were cut from adjacent portions of a large crystal of aluminum which had been stretched by 20 pct, and all surfaces on both specimens were prepared metallographically. The two specimens then were placed side by side for 1 hr in a furnace at 445°C, one being subjected to a small tensile stress of 100 g per sq mm, and the other not stressed. The stressed specimen exhibited very strong surface rumplings as in Fig. 19, while the markings on the unstressed specimen were so feeble as to be scarcely visible; and this difference existed though the stress was too low to cause any trace of slip.

It is evident enough that slip is associated almost universally with the bend planes to which Dr. Jillson has redirected attention. This makes it interesting to speculate why they do not occur in certain specific cases, such as the extension of single crystals of zinc or cadmium, or of aluminum crystals of certain orientations.[56] I should be most interested to know Dr. Jillson's views on this problem.

Perhaps the cases just mentioned, and the instances of strongly developed deformation bands, are simply opposite extremes of a general process on the lines proposed by Dr. Jillson, i.e., in some cases deformation bands form cumulatively, in others they begin to form all the time but are constantly straightened out again. This view is strengthened by the observations that in an aluminum crystal stretched by, say, 30 pct, the strongly marked deformation bands are accompanied by numerous incipient bands which are too weak to be visible on the surface of the stretched crystals, but are rendered visible on the repolished surface by annealing.

Dr. Jillson's observations on twinning are also most elegant and striking. The thickness vs. time curves determined for the growth of deformation twins in zinc prompt several questions. Dr. Jillson accounts for the form of these curves in terms of an energy hump required to nucleate the twin which will grow catastrophically once it is nucleated because of the reduced

Fig. 19—Aluminum crystal stretched 35 pct, repolished and annealed 16 hr at 435°C (under a stress of 35 g per sq mm). X30.

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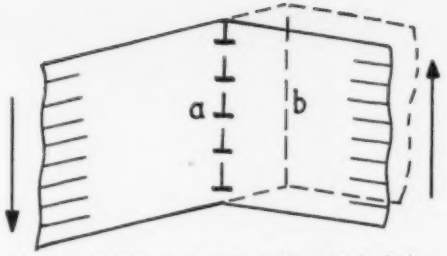

Fig. 20—Initial (a) and final (b) position of a bend plane subjected to a shear stress, schematic.

resistance to growth. The gradual slowing down of the growth in thickness is held to be due to the progressive relief of the stress which brought the twin into existence. But this view implies the use of a stiff spring to apply the force (a vice is effectively equivalent to this), the force in which is reduced as the specimen gives way. On the picture as stated, a twin should grow continuously to an unlimited extent under conditions of dead loading, for then no amount of twinning can relieve the stress, and a particular twin might be expected to continue growing more readily than another would be nucleated. At any rate, it would be expected that the thickness vs. time curve would have a different form in this case. It is an observed fact, however, that twins do not usually exceed a limiting thickness which varies with the particular metal. If this is followed up, it becomes apparent that there is a rough correlation between the characteristic widths of deformation twins in various metals and the shears associated with them. Thus in bismuth and tin in which the twins undergo a very small shear (s = 0.118 and 0.120, respectively), very coarse twins, a large fraction of a millimeter across, can be produced; while in α iron, the twins, for which s = 0.707, never exceed a few microns in width, and in the face-centered cubic metals, for which the shear would be the same, deformation twins are chimeras, heard of but not seen. Now the higher the amount of shear, the more closely the atoms are forced together during the shearing process itself, and the higher the energy barrier to be overcome. It may well be that in the catastrophic first stage of the growth of a twin, cumulative strains are generated in the parent crystal adjacent to the growing twin and in the twin itself, and it may well be those stresses which set a limit to the growth of the twin. Other factors also will contribute to determining this limiting width (e.g., the closeness to which the twinning process approximates to a pure shear, which in turn depends on the crystal structure) and the correlation between this width and the shear is not perfect. Thus neither of the types of deformation twins in uranium (with shears of 0.299 and 0.213) ever exceed a few microns in width, though the shear is considerably less than for iron.

Another question which occurred to me is whether, when a twin is formed and destroyed repeatedly by reversing the stress, the twin always appeared in exactly the same plane and grew to the same thickness for a particular stress. If this was so, it would imply either that not all vestiges of the twin disappeared during the reverse cycle (i.e., that the twin nucleus is as difficult to erase as it is to create), or else that the twin forms at a place where the lattice is disturbed prior to the application of the stress. Furthermore, the occurrence of bend planes at the tip of a lenticular twin, as sketched in Fig. 12, should lead to a building up of permanent strain in the crystal on reverse cycling (unless indeed the formation of such bands is perfectly reversible), and this might be expected to affect the appearance of the twin as the number of cycles increased.

Finally I should like to ask Dr. Jillson how he was able to detect the very interesting instances of bend

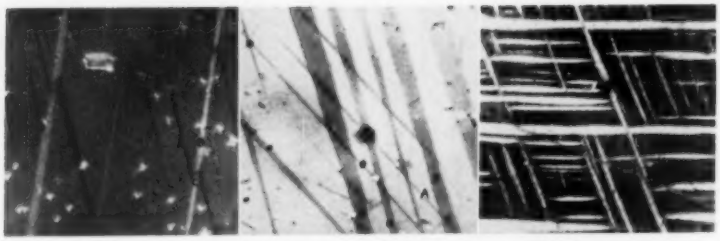

Fig. 21 (left)—Deformation twins in uranium section. Polarized light. X1500.

Fig. 22 (center)—Deformation twins in uranium section. Polarized light. X1200.

Fig. 23 (right)—Deformation twins in uranium section. Polarized light X1200.

planes being associated with twin tips and intersections, Fig. 12. These observations go some way towards explaining something which has puzzled me for a long time, namely, how a lenticular twin can be formed at all. However, the bands must surely be extremely faint—I have certainly never been able to detect any at the extremities of twins in deformed uranium, though I am very ready to believe that they are there. It may incidentally be of interest to record here that places where twins intersect or abut on each other are not necessarily places of high strain. Figs. 21 and 22 show two fields in compressed grains of uranium, in which two families of twins cross each other with a fine disregard for each other's presence; this may be compared with Fig. 23, showing a different pair of twin families again, in which most of the twins stop short of each other in the way familiar in, say, bismuth. In the case of the smooth intersections, twins *A* and *C* intersect along a line lying in the plane of twin *B*, and moreover the direction and amount of shear is the same in both *A* and *C*. In the case of Fig. 21, this direction coincides with the intersection of *A* and *C*, and we have a phenomenon directly analogous to cross-slip, i.e., cross-twinning. Here twin *B* is formed by a shear of the first type.[6] In the other case, twin *B* is formed by a shear of the second type.[6] When the conditions mentioned above did not apply, the characteristic appearance of Fig. 23 was encountered.

I trust Dr. Jillson will forgive the somewhat disjointed nature of these remarks, which are put forward in the hope that they may return a tiny fraction of the stimulation which I have found in his own paper.

D. C. Jillson—The questions raised in your second and fifth paragraphs are answered, of course, in your sixth paragraph. I see no inconsistency between the formation and removal or flow of very slight, highly submicroscopic bends under stress and the piling up of such minute bends at a barrier of one kind or another to form a detectable bend. They might also pile up if conditions were such that the rate of formation exceeded the rate of flow. After the pile-up reaches a certain size, it might itself, as you suggest, present a barrier. I expect that in cases where deformation does not seem to result in bend planes we can assume that coalescence or piling up has not progressed to a point where the bends can be detected. If we were to deform a sufficiently perfect specimen under suitable conditions, piling up or large bends might be avoided, and bend planes might never be detected. Bend planes most certainly have been observed in single crystals of zinc extended under other conditions.

The problem is the same if you are thinking in terms of dislocations. To supply the number of dislocations required to account for plastic flow, assumptions of generation at the surface, or of reflection, or of multiplication have been made. I suggest that rumpling may afford a mechanism for the generation of dislocations within a crystal and that there seem to be reasons for giving serious attention to this possibility.

In regard to the thickness of mechanical twins, I expect that in the unattainable case of a perfect crystal in a perfect setup, such that a single twin might form and grow without restraint and without the introduction of any other deformation, dead loading would cause unlimited growth without the nucleation of another twin. The rough correlation between widths of twins and the shears associated with twinning is probably a result of constraints, and I would expect the width of twin for a given metal to vary with the conditions determining the degree of constraint.

The question of whether a twin recurs on exactly the same plane upon repeated twinning and detwinning could not be answered experimentally because other deformations were always introduced. Had the specimen been perfect and had no other deformation been introduced, the shearing should have started between the planes where the stress was the highest, and if the experiment could have been carried out perfectly, this should have been the same place every time.

The specimen represented in the bottom sketch in Fig. 12 was obtained by compressing a smooth cylindrical specimen in which the basal plane was perpendicular to the specimen axis. The resultant markings were quite clear on the cylindrical surface. The markings of the middle sketch, too, were clear enough on the smooth surfaces of a deformed specimen of square section. The nature of the markings shown in the top sketch was deduced from observations of the markings on basal faces cleaved before the specimen was twinned. It was noted that if the twin went all the way through the specimen, there was no adjacent bend, but that if the twin did not, being then of a presumably lenticular shape, there was an adjacent bend in the surface. The sketch represents what we believe to be a logical rationalization. We did not observe this on a polished section such as shown in the sketch because the actual bend was very slight. The difference in the reflection of light from the basal surface, however, was quite definite.

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A Study of the Plastic Behavior of High-Purity Aluminum Single Crystals at Various Temperatures

by F. D. Rosi and C. H. Mathewson

DISCUSSION, B. Averbach presiding

P. A. Jacquet (*Paris, France*)—The authors state on p. 1163: "It is known that the oxide film which forms very rapidly on electrolytically polished aluminum in contact with air has a disturbing effect on the appearance of slip bands, making them wavy rather than straight."

Actually the oxide layer which builds itself in the air on an aluminum surface electropolished in the proper way is extremely thin—it is not visible by electron diffraction as observed by H. Raether[29]—and cannot have any effect on the slip bands.

On the other hand it is well known that some polishing baths which contain fluoboric acid, phosphoric acid, nitric acid, etc., lead to the building up of a thick oxide layer during the polishing. Thus with such an electrolyte aluminum comes out of the bath already oxidized, whereas with a ClO_4H-acetic anhydride bath the metal is practically un-oxidized when taken out and then is covered rapidly with a 20A thick layer which subsequently grows very slowly.

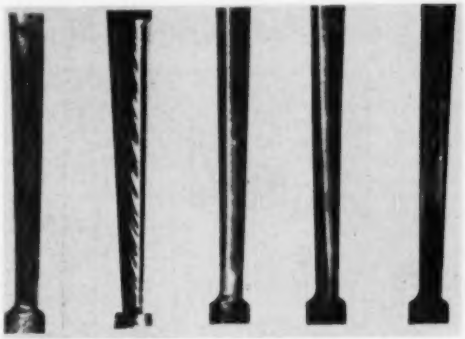
G. R. Wilms has shown that the thick alumina layers built up during polishing in the above-mentioned electrolytes hinder the observation of aluminum surface deformation. He determined also that the same cause of error does not exist with a metal polish in perchloric acid-acetic anhydride bath.

F. D. Rosi (authors' reply)—Dr. Jacquet is quite right in pointing out that the difficulty encountered in observing deformation markings is a direct result of the oxide layer developed during the electrolytic polishing. It was not intended to attribute the degree of thickness of the oxide layer entirely to specimen contact with the atmosphere. In fact, it was mentioned in the paper that "the nature of the oxide film depends to a great extent upon the electrolytic polish used, and perhaps unintentional variations in the technique of polishing." From the observed results, we strongly believe that the oxide film resulting from polishing in a methyl alcohol-nitric acid bath is not deleterious to the observation of slip markings in high-purity aluminum. Like Dr. Jacquet, we, also, have found that polishing in a fluoboric acid bath makes the examination of surface markings difficult.

N. K. Chen and **R. Maddin** (*Johns Hopkins University, Baltimore*)—The results recorded in this paper are very interesting; in particular, we would like to refer to the authors' Fig. 10, in which is shown the effect of increasing strain on the density of slip bands in the early stages of plastic flow. Although it is apparent from the curves that the orientation of the crystals has a marked effect on the density of slip bands for a given amount of strain, no particular orientational relationship seems to have been established.

One of the discussers (N. K. Chen) has made a structural study of aluminum single crystals of many orientations after plastic extension. Most aluminum single crystals exhibit slip lines with a reasonable regularity of spacing, together with deformation bands. However, there is an area of orientation, spreading out from the <111> pole of the Taylor and Elam triangle, in which flexual gliding seems not to occur and slip lines are spaced much more irregularly, assuming a strongly clustered appearance,[30] Fig. 23. By simple comparison it is apparent that crystals with clustered slip lines will give a smaller density of slip markings upon measurement.

Thus it is noticed that in the authors' Fig. 10 crystals *G* and *E*, which exhibit a much smaller number of slip bands per mm than the crystals *T* and *H* at the same amount of strain, are both oriented with their stress axes near <111>, the particular area discussed above. Since strain hardening did not appear to vary with the orientation of the crystal, and thus could not be used as a clue in this case to explain such fundamental difference of the appearance of slip bands, the nature of lattice rotations, such as the generation of deformation bands, and operations of conjugate and cross-slip systems, may be considered as one probable cause.



A7	A3	A15	A12′	A6
λ = 35°30′	λ = 36°	λ = 37°30′	λ = 43°	λ = 41°30′
χ = 25°00′	χ = 27°30′	χ = 36°30′	χ = 42°	χ = 40°00′

Fig. 23—Effect of orientation on distribution of slip bands on extended tapered aluminum single crystals. X1.

For example, it has been shown by Heidenreich[31] that in aluminum the glide lamellae are about 200A thick and have been displaced about 2000A. For equal amounts of strain it would appear that the displacement of lamellae must vary if the density of the slip bands is to change with the orientation.

If crystals such as the authors' *G* and *I*, extended the same amount, are to have a vastly different density of slip bands, then either the displacement of the bands in the different crystals in question must vary or other factors such as the action of collateral slip systems and the formation of deformation bands retard the classical lattice rotation of one of these crystals (the one having the greater number of slip bands), so that both result in the same amount of strain.

F. D. Rosi—The observations of Drs. Chen and Maddin on the change in the character of slip markings for a specific orientation might account, in part, for the differences found in the density of slip bands for crystals of different orientation. It would be interesting to know more details regarding the nature of the clustering; for example, if it is similar to that observed in α brass crystals. On their basis, however, it is difficult to explain the similarity in density of slip bands (particularly for small strains) between crystals *E* and *H*, which have markedly different orientations. The character of the slip bands in these two crystals (as well as in crystal *A*) were quite similar; and, in contrast to crystal *T*, they appeared thicker and did display a minor tendency for dense clustering in some regions. Furthermore, in crystal *T* there was a greater evidence of the segmented type slip, reported and described in the paper as characteristic of deformation at lower temperatures. In view of the recent electron microscope studies of slip bands by Heidenreich and Shockley,[31] these observations do suggest that the amount of shear per slip band in crystals *E*, *H*, and *G* is greater than in *T* for a given amount of extension.

Recent experiments on single crystals of different metals at Sylvania Laboratories suggest a correlation between the nature of slip markings and changes observed in the shear hardening curve in regions of small plastic strain. These results also have emphasized a

definite need for more systematic and detailed studies of the nature of slip markings in single crystals possessing critical orientations.

C. Crussard (*Ecole des Mines, Paris, France*)—It is a very interesting fact that the aluminum crystals prepared by the authors by solidification display the same properties as the one I have made by recrystallization, regarding the discontinuous or steplike formation of slip bands.

The shape of the stress-strain curves observed by the authors on their crystals is also very similar to that of our recrystallized single crystals,[6] when only one glide system is active at the beginning. After 1 pct elongation, the new rise in our curves has been related by us to a strong increase in asterism and to the formation of deformation bands. It would be interesting to know if the same rise in the curve exists for the authors' crystals. In the case where two glide systems are active right from the beginning, we have observed a different shape of the stress-strain curve: It is parabolic from the beginning as has been postulated by G. I. Taylor; the asterism is stronger at the beginning than in the general case, but weaker at about 10 to 20 pct elongation, because no deformation bands are formed.

It is interesting to point out that the shape of stress-strain curves obtained by the authors on fused crystals seems in contradiction with the well-known experiments of Dehlinger and Gisen. The latter seems also in contradiction with some newer observations regarding the state of perfection of the crystals as shown by A. Guinier and myself.[6] Thus, it would be extremely interesting to have some X-ray information on the crystals used here by the authors, regarding the state of perfection of each of the subgrains of the lineage structure, for orientation (e.g. by Guinier's method) and intensity of reflection.

F. D. Rosi—Dr. Crussard's comments are both interesting and gratifying. It is significant to find that aluminum single crystals of similar purity produced by critical recrystallization show properties similar to those prepared by solidification from the melt. If structural irregularities are at the bottom of most plastic phenomena observed in real metals, then there can be no serious difference in the imperfections resulting from these two modes of single-crystal production of high purity metals.

With regard to a change in the shear hardening of these stress-strain diagrams, we also have observed a gradual rise in the curves at room temperature after an extension of about 0.4 pct. However, this value of extension appeared to vary with orientation, being somewhat less for those orientations nearer the [100] and [111] poles. At the temperature of liquid nitrogen this change of slope was not observed. Recent experiments on the extension of high purity silver single crystals (to be published) show a similar, but more marked inflection in the shear hardening curve after small amounts of extension (approximately 0.7 pct). Furthermore, a temperature dependence of this unique behavior has been fairly well established.

The extent of the X-ray studies was confined to ordinary back-reflection photograms, which were taken at various points along the circumference of the specimen. In general no asterism was observed up to extensions of approximately 1.5 pct for the room temperature tests. In view of the X-ray techniques used, no detailed study of structural imperfections in these crystals was possible. The only evidence of structural irregularities was the occasional presence of double diffraction spots indicative of the lineage imperfections. As mentioned in the paper, the angular spread of these spots was never observed to exceed 2°.

It appears that the essential difference in the stress-strain diagrams reported by Dehlinger and Gisen on aluminum crystals prepared by solidification and those of the present investigation is in the sharpness of the yield point. In the case of the former, the yield point was ill-defined, which might very well be attributed to the lower purity of the metal, for, perhaps, the same reason that the yield point becomes less accentuated with decreasing temperature. Furthermore, it is quite possible that this same effect of increasing purity may be responsible for the rise in the stress-strain diagram after small extensions reported in the present investigation, but not observed by Dehlinger and Gisen in the less pure material.

W. C. Ellis (*Bell Telephone Laboratories, New York*)—Important new information for plastic behavior at several temperatures was reported in this paper for tests carried out with a nearly constant rate of stressing. Similar work has been done by other investigators using a constant strain rate. When a constant stress rate is used the strain rate is not necessarily constant over the range of a single test and usually is not. However, as shown in Fig. 5 of the paper, the strain rate is essentially constant in the plastic range for the individual tests. For tests at different temperatures, however, the strain rates are appreciably different, being substantially higher for the tests at 353°K. The importance of strain rate would seem to be that the recovery processes, being time dependent, are linked to the rate of straining—a faster rate permitting less recovery. Recovery in these tests would have been influenced not only by the different temperatures used, but also by the different strain rates. The latter may have been only minor although we do know that recovery proceeds (at least to some degree) in high purity aluminum at quite low temperatures. I should like to ask the authors to what extent they believe a varying strain rate may have affected the results and what the strain rates were in the tests?

F. D. Rosi—Dr. Ellis' question as to the effect of different strain rates at the different temperatures of testing on the results reported in this paper is indeed one worthy of consideration. It has been fairly well established that the speed of stressing has an insignificant effect at low temperatures and near the melting point, but a rather marked influence in an intermediate range of temperature. As Dr. Ellis points out, for aluminum of such high purity, this temperature range, where time effects are important, might very well be from room temperature to 200°C. Nevertheless, in view of previous investigations on the effect of strain rates on such fundamental properties as the critical shear stress and the coefficient of shear hardening, it appears very unlikely that this factor would affect these properties to an appreciable extent under the conditions of the present investigation, where the strain rate only varied by a factor of 5 over the temperature range of testing, see Table V. For example, in tests on aluminum at room temperature Weerts[6] found that on varying the speed of testing from 1:23,000 (450 pct elongation per sec) glide began at approximately the same stress, and the shear hardening increased by only 16 pct. In fact, even for hexagonal metals where this effect of varying strain rates appears to be more significant, a hundred-fold increase in the speed of testing is necessary to produce an increase in the critical shear stress of 20 to 30 pct. As corollary evidence, very recent experiments with high purity (99.99 pct) silver single crystals showed that a two-fold increase in the speed of stressing (for rates comparable to the experiments with aluminum) showed no change in the values for critical shear stress or coefficient of shear hardening.

Table V. Variation of Strain Rate over Temperature Range Tested

Testing Temperature, °K	Mean Strain Rate, Strain per Min
77	8.2×10^{-4}
205	4.1×10^{-4}
295	2.7×10^{-4}
353	1.7×10^{-4}

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A Study of the Strain Markings in Aluminum

by Bani R. Banerjee

DISCUSSION, B. Averbach presiding

R. G. Treuting (*Bell Telephone Laboratories, New York*)—The author is first to be congratulated on a careful technique that has demonstrated the occurrence in aluminum at low temperatures of the strain markings observed in other face-centered cubic metals at normal temperatures, and the thermal instability of these markings.

In view of his findings, the author's hypothesis that either a stacking fault or an extended dislocation introduced by low temperature deformation has an associated energy higher than in other face-centered cubic metals is, as he says, logical, and worthy of some further comment:

1—The ratio of twin interface tension to grain boundary tension in aluminum has been found to be significantly higher than in copper.[11] To the extent that the respective grain boundary tensions are comparable, the twin interface tensions differ correspondingly. This would presumably apply in similar degree to twin faulting. Barrett[12] has also concluded from X-ray line width data that the faulting energy of aluminum is large.

2—R. D. Heidenreich[13] has found by electron microscopy that polygonization[14] of deformed aluminum occurs at the temperature of liquid nitrogen, —196°C. Hence the recovery process proceeds at the temperature of the present experiments, —72°C, probably at a significant rate.

3—There is evidence, e.g., Maddin, Mathewson, and Hibbard[7] that recrystallization twin bands are aligned with previous slip lines. This has been interpreted as indicating that slip generates twin faults in accordance with Mathewson's hypothesis. However, recent work by Burke[15] suggests strongly that twin faulting from slip cannot be the only source of twin bands observed in substantially recrystallized metals. The absence of twin bands in recrystallized aluminum may require further explanation than the thermal relief of twin faulting.

It would seem that a critical experiment is still needed to determine whether twin faulting is produced by slip. The method employed by Barrett[16] to establish stacking disorders in the Cu-Si system may profitably be applied to deformed metals, if a sufficient proportion of presumptively faulted planes can be generated without introducing so much lattice distortion as to obscure the X-ray data. This might be accomplished by a deformation mechanism permitting continuous or periodic shifting of the applied stress axis to maintain the pole of the latter within a single stereographic triangle of the single-crystal specimen projection.

The writer is indebted to his associates W. T. Read and R. D. Heidenreich for helpful discussions with respect to these comments.

P. A. Jacquet (*Paris, France*)—For the first time we succeeded in detecting "strain markings" far below the surface of a copper specimen which had been deformed by as small an amount as 1 pct in extension.[17] The observations of these markings is solely due to the sensitivity of the etchant. Thus with brass and other copper alloys a sodium hyposulphite electrolytic etch is far more sensitive than any other etch by known standard reagents.[18] With copper the most sensitive method is a short-cut etch into the electropolishing bath (phosphoric acid).

With aluminum bronze, some strain markings seem to correspond to microtwins, Fig. 6. With brass, the etch (Fig. 7) probably shows the regions where there are numerous whole sets of gliding lamellae which

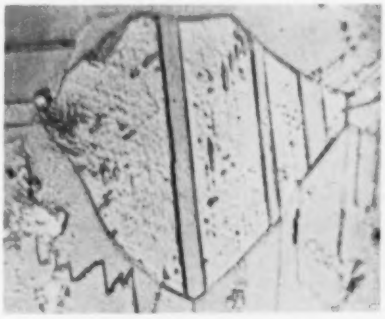

Fig. 6—Aluminum bronze annealed plate. X1600.
Surface abrased with emery paper No. 1. Electrolytic polishing to dissolve 15 micron thickness. Anodic etching in sodium hyposulphite at 0.4 pct. Strain markings show up as parallel striation systems oriented at 60°, on which a little element—which seems to be microtwins—can be seen.

form each slip line visible on the polished surface before etching.

The author stresses the importance of avoiding any heating for strain-marking observations, for instance mechanical polishing is performed by frequent coolings of the specimen down to —72°C. But it is certain that during electropolishing a substantial superficial heating takes place, especially in the process described with No. 1 electrolyte where the current density is of the order 100A per sq decimeter.

Even with electrolyte No. 2 (described as $HClO_4$-acetic acid in the footnote, p. 1126, and $HClO_4$-acetic anhydride in Table I) an increase of the temperature exists. How does the author reconcile these two contradictory features?

B. R. Banerjee (author's reply)—The author is indebted to Dr. Treuting for his interesting comments, particularly for pointing out some recent experimental results tending to substantiate the author's hypothesis.

The author would also like to thank Dr. Jacquet for

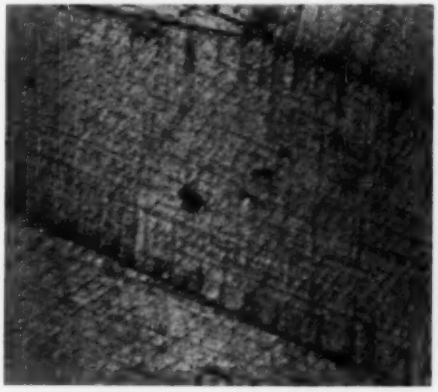

Fig. 7—Annealed α brass. X1600.
Surface abrased with emery paper No. 2, then electropolished (dissolution 0.24 mm), final anodic etching in 0.1 pct sodium hyposulphite solution. The lower distinct diagonal line is a twin boundary.

his remarks. Although a small local heating undoubtedly does occur during electrolytic polishing, the constant contact with the cool electrolyte, and the short duration of polishing time, presumably help to keep the temperatures sufficiently low to prevent excessive recovery.

The author would like to correct the discrepancy pointed out by Dr. Jacquet. The electrolyte No. 2 was perchloric acid and glacial acetic acid.

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[16] C. S. Barrett: *Trans.* AIME (1950) **188**, p. 123; JOURNAL OF METALS (January 1950).

[17] P. A. Jacquet: *Comptes Rendus* (1944) **218**, p. 790; *Rev. Metallurgie* (1945) **42**, p. 133.

[18] P. A. Jacquet: *Comptes Rendus* (1949) **228**, p. 1029; *Rev. Metallurgie* (1950) **47**, p. 355.

Activation Energy for Recrystallization in Rolled Copper

by B. F. Decker and D. Harker

DISCUSSION, R. Maddin presiding

F. H. Wilson *(American Brass Co., Waterbury, Conn.)*—The authors are to be congratulated for employing a simple and direct technique for measuring the extent of recrystallization. By this method they are sure that they are determining the activation energy for recrystallization alone, uncomplicated by strain relief or other effects associated with recovery which hamper interpretations when the changes in other quantities during annealing are measured.

They tacitly assume that only the orientations which constitute the deformation texture and the "cubic" recrystallization texture are involved, and this assumption is related directly to the question of the origin of recrystallization textures concerning which opinions are still in conflict. It would be expected that their specimens showing maximum intensity from (200) planes reflections, having been rolled 98 pct, would have microstructures which show them to be 100 pct in the cubic orientation. Did they confirm this? Assuming this to be true, it would appear to be possible to employ the authors' data to determine whether the recrystallization texture resulted from "oriented nucleation" or from "oriented growth."

The value for the percentage of material transformed as derived from measurements of loss in intensity of (111) reflections would be independent of the orientations of the transformed material (except for the remote possibility that an appreciable number of the new nuclei would have [111] poles oriented the same as the deformation texture). However, the value as derived from measurements of gain in intensity of (200) reflections would depend upon whether the nuclei were all in the "cubic" orientation or whether other orientations formed. The values as derived from both sets of measurements would be equivalent throughout only if the nuclei formed in the "cubic" orientation. If values derived from (200) reflections are consistently lower at the start of recrystallization than those derived from (111) reflections, there would be some support for the theory of "oriented growth."

It would be of considerable value in contributing to our understanding of the mechanism of recrystallization if the authors could submit data to show the extent of agreement between the two sets of intensity measurements.

M. Balicki *(Polytechnic Institute of Brooklyn, Brooklyn, N. Y.)*—In 1937, A. Krupkowski and M. Balicki determined the activation energy for recrystallization of cold deformed copper[5] from both isothermal and isochronal experiments on cold-drawn commercial copper, using the change in mechanical properties as an index of structural changes. The values then obtained (32 and 31.5 kcal per mol) within the limit of accuracy, are identical with the figures obtained by the authors for OFHC copper (29.9 kcal per mol). M. Cook and T. L. Richards[6] in 1946 obtained values for the activation energy for copper of the order of 43 to 48 kcal per mol that are different from the values found by the authors and in ref. 5 because of the employment of a different formula. It has been shown, however, that the isochronal annealing experiments performed by Cook and Richards yield values between 30.4 and 32.4 kcal per mol,[7] if treated by the method of Krupkowski and Balicki.[5] These figures compare well with the ones reported in the present paper for OFHC copper.

L. R. Jackson, A. M. Hall, and A. D. Schwope[8] used a value of 30 kcal per mol for the activation energy for the recrystallization of copper and the treatment of Krupkowski and Balicki to predict successfully the prolonged isothermal annealing behavior of various commercial grades of copper from the experimental data of short duration isochronal annealing.

The method adopted by the authors for heat treating isothermally is limited to relatively short times performed at relatively high temperatures, since changes in barometric pressure during prolonged treatments will affect the boiling points of the liquids used as an annealing medium and cause a fluctuation in the temperature. Did the authors perform their anneals at times when the barometric pressure was the same and did they note any deviations from the nominal annealing temperature by direct measurements? The quite feasible slight deviation from the nominal annealing temperatures would materially affect the location of the experimental points in Figs. 1, 2, and 4, so that the curves (with the exception of the last one in Fig. 4) might not give a true picture of the progress of reannealing, and the two middle curves in Fig. 4 might be curved due to this cause.

Finally, the method is based on the assumption that during the recrystallization there is a change in orientation. As far as I know there is no proof that recrystallization will always bring about a different orientation from that of the cold deformed matrix. The accuracy of the method, therefore, will depend upon many factors which influence texture formation and will vary from case to case, such as: 1—Degree and character of impurity atoms present, 2—amount and character of alloy elements present, 3—the degree of cold work, 4—the mode of plastic deformation, 5—grain size and randomness produced by penultimate anneal, and 6—susceptibility to self-annealing during cold deformation and subsequent storage. Thus, a question arises about the accuracy of this new method and whether or not the degree of accuracy is the same for both types of copper tested. As a consequence, one is left wondering whether the differences in activation energy of 29.9 and 22.4 kcal per mol found by the authors are real or due to the systematic error of the method.

B. F. Decker (authors' reply)—Dr. Wilson's suggestion that knowledge of the agreement between measurements of the appearance of recrystallized material and the disappearance of cold-worked material would contribute to an understanding of the mechanism of recrystallization is well taken. The authors have not correlated data of this type for copper. However, Seymour and Harker[9] in their studies of 50 Fe 50 Ni alloy did

obtain both kinds of data. Their results are shown in Figs. 1 and 2 of their paper. For a given time and temperature there is good agreement between values obtained by the two methods for amount of material recrystallized. This would rule out the possibility that the texture sharpened by ordinary grain growth after recrystallization.

No microstructural investigation was made of the copper samples studied.

The authors thank Dr. Balicki for his interest in and comments on this paper, but they believe that his criticism of the accuracy of the method is not justified. All heat treatments in the boiling organic liquid at any one temperature were made on the same day, and temperature checks were made frequently with a calibrated thermometer. A temperature shift greater than 0.5° was never found and shifts of 0.5° only rarely. Consequently, the accuracy of the experimental points in Figs. 1, 2, and 4 is not affected materially by the method of annealing, and the shapes of the curves in Figs. 4 and 5 are real.

The authors admit that this method is not applicable to cases of recrystallization without change in orientation. However, primary recrystallization in copper is not such a case.

In reply to Dr. Balicki's suggestion that the difference in activation energy of 29.9 and 22.4 kcal per mol is due to error in the method, analysis of the data shows that the maximum deviation of Q for the pure copper is 1.1 kcal per mol and for the OFHC copper 1.7 kcal per mol. Therefore, the maximum experimental uncertainty (2.8 kcal per mol) in the difference in activation energy for the two kinds of copper is very much less than the measured difference of 7.5 kcal per mol.

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Recrystallization Reaction Kinetics and Texture Studies of a 50 Iron 50 Nickel Alloy

by William E. Seymour and David Harker

DISCUSSION, R. Maddin presiding

A. A. Burr *(Rensselaer Polytechnic Institute, Troy, N. Y.)*—I would like to say a few words about this interesting method of applying the X-ray spectrometer to measuring structural changes in metals. As the authors of both papers just presented[a] have pointed out, the success of the method depends on the fact that: 1—The spectrometer when set up as described, measures diffracted energy only from planes parallel to the face of the specimen. 2—A high degree of preferred orientation exists in the specimen initially and a change in grain orientation occurs as the process under study proceeds.

I would like to point out another metallurgical problem where the same principles have been utilized. In some work done in 1943 at the Pennsylvania State College[b] involving the interdiffusion of thin films of copper and zinc, an analogous setup was used to follow the diffusion process and to verify the Widmanstätten relationships between the phases in this system. In this case the zinc film exhibited a high degree of preferred orientation with the basal planes parallel to the glass substrate. As the structure changed with diffusion at relatively low temperatures the breakdown of the zinc structure and the growth of that of β brass could be followed. From the preferred orientation of the resultant brass the Widmanstätten orientation relationships could be determined.

W. E. Seymour and **D. Harker** (authors' reply)—We are very grateful to have been reminded by Professor Burr of the work done by him and others at Pennsylvania State College, using X-ray diffraction methods similar to ours; our failure to give reference to this work was due entirely to oversight.

[a] This refers to paper by B. F. Decker and D. Harker, the discussion of which is on p. 548, this volume, and this paper.

[b] Burr, Coleman, and Davey: An X-Ray Study of Brasses Formed by the Interdiffusion of Copper and Zinc Deposited on Glass by Vaporization. *Trans.* ASM (1944) **33**, p. 73.

The Textures of Cold-Rolled and Annealed Titanium

by Howard T. Clark, Jr.

DISCUSSION, R. Maddin presiding

M. K. Yen and **J. P. Nielsen** *(New York University, New York)*—We wish to compliment Dr. Clark on his excellent work and interesting results. The double texture reported in this paper was found to be in good agreement with our results on iodide titanium after 97.75 pct reduction by cold rolling.[c] The rolling texture was characterized by a clustering of the (0001) poles around two axes lying in the transverse plane and inclined at 30° to the rolling plane. The average grain orientation for the specimen could be shown schematically as in Fig. 4. Moreover, this double texture also was found in iodide titanium deformed by compression. The usual [0001] compression texture occurring in h.c.p. metals was observed for reductions up to about 85 pct. However, a pronounced double texture comparable to that shown in Fig. 1c of Dr. Clark's paper was obtained when a specimen was subjected to compression rolling totaling about 94.5 pct. The difference in preferredness between the center and the surface material in compression rolled specimens also was studied. The results

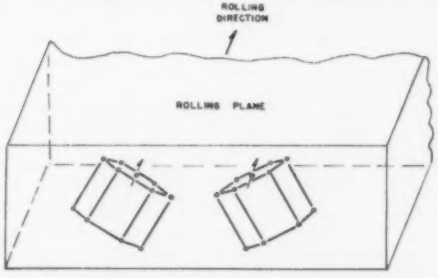

Fig. 4—Schematic diagram of average grain orientations of α titanium after a reduction of 97.75 pct by cold rolling.

Table II. Types of Pole Figures for Various Rolled Close Packed Hexagonal Metals

Metals	C:A Ratio	Type of Scattering	Reference
Zn	1.856	20°-25° toward rolling direction	Caglioti and Sachs[9]
Cd	1.885		Valouch[10]
Mg	1.624	i. Equal scattering	Schmid and Wassermann[11]
		ii. Slightly toward rolling direction	Bakarian[2]
Zr	1.590	Scattering toward transverse direction	Burgers and Jacobs[1]
Ti	1.587		Clark,[12] Yen[8]
Be	1.568		Smigelskas and Barrett[3]

obtained were similar to those of Dr. Clark on straight rolling, i.e., the center material had a more pronounced double texture than did the surface material.

In the case of wires by rolling for 85 pct reduction in area, the following planes were found to lie perpendicular to the wire axis, in the order of prevalence: (1010), (1011), and (0001). A relatively sharp [1010] texture was observed in a wire specimen reduced 92 pct in area.

If we make a correlation of the type of distribution of the basal planes in the pole figure with c:a ratio, as in Table II, we find that the first group, Zn and Cd ($c:a > 1.633$), has a scattering toward rolling direction and that the third group, Zr, Ti, and Be ($c:a < 1.633$) has a scattering toward transverse direction. In the case of Mg, the c:a ratio is quite close to 1.633, and it exhibits both directions of scattering although a scattering tendency has been reported similar to that of the Zn and Cd group. The variations in the reported Mg results may be accounted for by slight changes of c:a ratio around the ideal 1.633 value due to the presence of impurities.

The scattering in the rolling textures of the metals listed in Table II may be related to twinning as well as to the c:a ratio. For Zn and Cd, twinning results in elongation along the twinning direction and for Zr, Ti and Be, twinning produces a shortening in the twinning direction. For the first group the flow of metal would be assisted by twinning along the rolling direction and thus twinning might be related to the scattering toward the rolling direction. Dr. Clark has pointed out that twinning on the (1102) planes of Ti would yield a thickening of the metal. However, since twinning in Zr, Ti, and Be produces a shortening which is inconsistent with the flow of the metal, its relative occurrence would be greater in the transverse direction than in the rolling direction. This type of twinning then would be related to the observed scattering toward the transverse direction.

It is also interesting to note that at certain orientation at which the twinning plane in h.c.p. metals is parallel to the rolling plane, e.g., the basal plane of Ti makes an angle of 42°30′ with the rolling plane, twinning may occur with no change in thickness of the metal.

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Production and Examination of Zinc Single Crystals

by D. C. Jillson

DISCUSSION, R. Maddin presiding

A. J. Goss and **S. Weintroub** *(University College, Southhampton, England)*—We have read Dr. Jillson's paper with considerable interest, particularly as we consider any detailed information with regard to the growth of metal crystals of extreme importance. Recently we have carried out a similar comprehensive investigation of the influence of temperature gradient and rate of growth on the successful production of single crystals of tin. A brief report of the results obtained will appear shortly in *Nature*. Andrade and Roscoe's method[12] with a horizontal traveling furnace was used, and the crystals were grown from the melt, in vacuo, in pyrex glass tubes. More recently we have turned our attention to zinc, and the results of our preliminary experiments on 99.95 pct purity Zn may be of interest. Each specimen of zinc before crystallization was in the form of a cast rod 25 cm long and 5 mm diam and was contained within an open pyrex glass tube of approximately 7 mm internal bore. The specimen and its surrounding glass tube was placed inside the furnace tube where a vacuum of the order of 10^{-5} mm Hg was maintained, during the process of crystallization. Various speeds of growth and temperature gradients were tried. The yield of good single crystals was 13 out of 15 specimens, 3 out of 11, and 0 out of 9, for 0.5, 1.5, and 5.3 mm per min speeds of growth, respectively. In the imperfect specimens the structure usually consisted of several parallel separate crystals along the length of the rod. It should be noted that the slowest speed used, namely 0.5 mm per min is slightly greater than that corresponding to 8°C per in. and 7.4°C per hr for which Dr. Jillson obtained 100 pct yield.

It is stated by Dr. Jillson that preferred directions of crystal growth in zinc crystals may be influenced by very small amounts of impurities. For 99.99+ pct pure Zn he found a preference for the basal planes to be within 20° of the perpendicular to the specimen axis; but for 99.999+ pct pure Zn, they were randomly orientated. We have found that for 99.95 pct Zn there is a marked preference for the angle between the c-axis, [001], of the successfully grown crystal and the specimen axis to be 70° to 90°. From suitable test temperature measurements that we have taken, it would appear that the direction of heat flow is along the specimen axis. It would be desirable to test further whether impurities are a controlling factor on the orientation, and we are extending our experiments to purer zinc.

The opinion has been expressed by those who have used methods for the production of metal single crystals in which the metal is held vertically, that the pressure of the superincumbent metal does not affect the crystal growth. However, we believe that this is still a matter of some doubt and would question whether, in addition to the proper direction of heat flow and impurity content, the presence of some 20 in. of superincumbent metal as in Dr. Jillson's case is not also a determining factor affecting the growth and possible orientation of the single crystal.

For the determination of the orientations of our zinc single crystals, we use the optical reflection method described by Chalmers,[13] and we have found that the thermal etching due to the normal vaporization of the crystal gives sharper reflection patterns than any of the chemical etchants mentioned by Dr. Jillson. We would recommend the use of the thermal etching. Nevertheless we do regard Dr. Jillson's results obtained by chemically etching the surface as of considerable interest and importance.

We would be glad to have more detailed data of the various speeds of growth and temperature gradients used by Dr. Jillson so as to check whether there is any relation between these two quantities and the yield of single crystals.

E. S. Greiner *(Bell Telephone Laboratories, New York)*—Crystal imperfections such as lineage result in

increasing the angular spread of back-reflection Laue spots. Since the ridges on the surface of the crystal shown in Fig. 5 of the paper may be evidence of lineage in the zinc, I wish to ask the author if he observed any significant difference in the angular spread of back-reflection spots depending on whether the X-rays were reflected from a ridged or a smooth area of the surface. Was there any change in the angular spread of corresponding Laue spots reflected from various areas of the crystal surfaces? This information would aid in evaluating the perfection of these zinc crystals.

G. Edmunds *(American Brake Shoe Co., Mahwah, N. J.)*—The author has observed a wide range of orientations of the single crystals produced from 99.999 + pct Zn and has suggested "a possibility that preferred directions of crystal growth in zinc crystals may be influenced by very small amounts of impurities." What seems to be a more likely explanation of the occurrence of random orientations is that the perfection of Dr. Jillson's experimental technique, together with the small content of impurities that might nucleate growth, has resulted in only one nucleus being a center of crystallization. Except insofar as nuclei might tend to be oriented preferentially, this should lead to randomness of crystal orientation. Under less perfect experimental conditions more centers of crystallization would be expected, and there would be a tendency for those crystals to survive and extend whose [210] direction (nearly[14] the direction of maximum growth rate) most nearly paralleled the direction of the maximum thermal gradient. Thus, it seems logical to expect more randomness of orientation in exceptionally pure metal, but not an influence on the preferred direction of crystal growth as suggested by Dr. Jillson.

D. C. Jillson (author's reply)—The data of Goss and Weintroub suggest better yields at lower growth rates, but do not show the separate effects of temperature gradient and cooling rate. A high cooling rate and temperature gradient can give the same growth rate as a low rate and gradient, but might give different results. We have not run enough tests with high or low temperature gradients or at high cooling rates to draw conclusions as to relative probabilities of success. We believe that success depends largely upon control of nucleation and that purity is a very important factor. With higher purity, the range of conditions for successful growth may be wider.

The data of Goss and Weintroub on orientation preferences in specimens of lower purity seem to support our own very meager data suggesting a possible influence of impurities on preferred direction of crystal growth. The arguments of Mr. Edmunds against this are very logical, but might be qualified to read "there would be a tendency for those crystals to survive and extend which have a direction of maximum growth rate (nearly [210] in zinc of 99.99 + pct purity or less) most nearly parallel to the direction of the maximum thermal gradient." Lacking definite data on growth rates in different directions in zinc of higher purity, and considering the present data and other data more recently brought to our attention, we feel that the question might be kept open.

We are sorry that we cannot answer Dr. Greiner's question regarding the angular spread of back-reflection spots from the ridged areas, because we prepared no back-reflection patterns of these areas. They were relatively lead-rich areas and we attributed the ridges to lead segregation.

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The Structure of Intermediate Phases In Alloys of Titanium with Iron, Cobalt, And Nickel

by P. Duwez and J. L. Taylor

DISCUSSION, B. D. Cullity presiding

E. S. Greiner *(Bell Telephone Laboratories, New York)*—In order to reveal the presence of ordering in alloy systems by the X-ray technique, the superlattice reflections must be of sufficient intensity for detection. If the scattering powers of the elements in the alloy are quite different, e.g., Cu-Au or Fe-Si, the reflections from the superlattice are intense and can be detected by usual X-ray procedures. If, however, the alloys are composed of elements whose atomic numbers differ by one or two, e.g., Cu-Zn, Fe-Co, or Fe-Ni, the superlattice reflections are very weak because of the small differences of scattering powers. In these cases it is necessary to select the radiation so as to obtain differences in scattering powers of the elements in the alloy, which are sufficient for the production of superlattice reflections. The method of selection has been described in the literature.[15]

The present paper describes X-ray tests which did not reveal ordering in Ti-Fe, Ti-Co, and Ti-Ni alloys, the atomic numbers of whose elements differ by 4, 5, and 6, respectively. I wish to ask the authors if one must select a favorable radiation to be certain of the detection of order, if present, in alloys such as these.

P. Duwez and **J. L. Taylor** (authors' reply)—It is true that by means of a proper choice of radiation it is possible to increase the difference between the scattering factors of two atoms in a crystal. This method, however, has not been used in the present investigation. It is therefore possible that very weak reflections were not detected on the X-ray diffraction patterns and more careful measurements might reveal the existence of an ordered structure in the TiFe, TiCo, and TiNi phases.

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On the Martensitic Transformation at Temperatures Approaching Absolute Zero

by S. A. Kulin and Morris Cohen

DISCUSSION, A. R. Troiano presiding

J. C. Fisher, J. H. Hollomon, and D. Turnbull *(General Electric Co., Schenectady)*—The authors have done an excellent piece of work in demonstrating that martensite plates form rapidly in stainless steel at a temperature of 4°K. According to the relationship:

$$\text{Rate} = \nu \exp(-Q/RT) \qquad [1]$$

an appreciable growth rate at 4°K corresponds to an activation energy Q of 100 cal per mol or so at the most. Using this argument, they have suggested that the atom-by-atom growth mechanism proposed for martensite probably is incorrect, and that a growth mechanism analogous to the propagation of sound waves is more likely.

The authors' observations are not in agreement with those of Kurdjumov and Maksimova, who report an activation energy $Q_m = 1600$ cal per mol for the growth of martensite in 0.6 pct C, 6 pct Mn steel, and near cessation of the martensite transformation below −200°C in this alloy. However, it may be possible to reconcile the two sets of observations.

The zero-point energy of a mol of crystalline solid is $E_0 = (9/8)\ R\theta_D$, according to the Debye model, where θ_D is a constant in the neighborhood of 10°.

This energy is split up among modes of vibration having energies varying from nearly zero to about (3/2) $R\theta_D$ cal per mol, raising a question as to the validity of eq 1 except for values of $Q > (3/2)\ R\theta_D$. For iron, $\theta_D = 420°K$, $E_a = 950$ cal per mol, and (3/2) $R\theta_D = 1260$ cal per mol. Hence, whenever Q is in the neighborhood of 1000 cal per mol in iron, the zero-point energy may be sufficient to allow the process to continue at 0°K by the tunnel effect.

If the activation energy Q_a for the unit process of the martensite transformation, thought of as an atom-by-atom process, is a function of composition, it may be possible to vary Q_a from a relatively large value where eq 1 is valid and Kurdjumov and Maksimova's observations could have been made, to a somewhat smaller value, less than the zero-point energy, where eq 1 may be invalid and the growth process could take on more of the characteristics of sound-wave propagation.

In order to check this hypothesis, it is necessary, among other things, to repeat the work of Kurdjumov and Maksimova, whose observations have not been reproduced yet despite earnest attempts by the authors. Although it is possible that Kurdjumov and Maksimova were mistaken in their observations, it is more probable that their published alloy compositions are in error, or that a misunderstanding of some sort exists concerning their procedure. These possibilities are being examined in a series of experiments being undertaken in our laboratory.

C. Crussard *(Ecole des Mines, Paris, France)*—The fact that martensite is formed at temperatures as low as 4°K is extremely interesting in itself; but in its interpretation there is need for care. At first glance, it seems to substantiate the theory of athermal nucleation of martensite, as no activation seems possible at absolute zero. But this conclusion is incorrect, because the theory of thermal motion generally accepted for solids is incorrect. I have shown elsewhere[1] that for transformation involving a simultaneous displacement of several atoms, the Boltzmann formula does not apply; the correct theory must take in account the interferences of thermal waves. A rough hypothesis has led me first to a formula of the type:

$$P = e^{-\sqrt{A\epsilon}} \qquad [2]$$

where P is the probability of activation, A an energy involving the shape of the nucleus, and ϵ the expression of the energy for a mode of vibration:

$$\epsilon = h\nu \frac{1}{2} + \frac{1}{e^{h\nu/kT} - 1} \qquad [3]$$

The active frequency, ν, depends also on the size of the nucleus; it is never far from the cutoff frequency.

A better, but still approximate calculation (to be published) leads to a more satisfying formula:

$$P = e^{-\frac{A}{\epsilon}} \qquad [4]$$

The formula holds also for single atoms.

Thus, activation is possible even at absolute zero (another possibility being the "tunnel effect" for electrons). The departure between the Boltzmann formula and the eq 4 is very difficult to test by experiment. Martensite transformation seems the best example. The author's experiments can be explained by eq 4, if it is assumed that martensite nucleates at quenching temperature.

The athermal nucleation theory, assuming martensite embryos to be formed at austenitizing temperature, actually meets very great difficulties:

1—If it is assumed that the embryos are produced by local fluctuations in composition of the alloy, the size-distribution curve of embryos is independent of temperature; thus stabilization of austenite cannot be explained. Moreover, the reverse transformation cannot be explained easily.

2—If it is assumed that the embryo is of the dislocation type, all the experimental facts do rather prove that dislocations stabilize austenite: On the other hand, M_s should strongly depend on the state of polygonization of austenite, a fact which has not yet been observed, to my knowledge.

It seems easier to explain stabilization of austenite by some kind of hardening in the austenite itself (some new experiments in my laboratory point to that result), which increases the stress-energy barrier to the transformation, because martensite cannot be formed without some kind of plastic deformation in the platelet or in the surroundings. Thus, there is no reason to reject the theory by which martensite is formed at quenching temperature, as is assumed by Scheil and others, according to the detailed mechanism of grouping of thermal waves which I proposed."

N. A. Ziegler and **P. H. Brace** *(Crane Co., Chicago)*—This very interesting paper, and particularly that part of it which deals with subzero transformations in 18-8 type steels, illustrates and rationalizes some of our observations."

One of the present discussers as early as February 1947 discovered that Charpy bars, made of certain austenitic stainless steel compositions, after having been fractured at the temperature of liquid nitrogen (about —300°F or —185°C), became, adjacent to the fracture, rather strongly magnetic. This increased magnetic permeability persisted at room temperature and apparently was caused by an (at least partial) transformation of the austenitic phase into ferritic.

This supposition was substantiated by hardness measurements taken close to the fracture ("magnetic" region), as compared to those taken away from the fracture ("nonmagnetic" region). The "near-fracture" hardness, at least in some cases, increased to values seldom observed in conventionally cold-worked steels of this type. Likewise, microexamination of "near fracture" regions disclosed structures very similar to that shown by the authors' Fig. 2b. None of these phenomena could be observed in the bars of similar compositions, but fractured at room temperature. Nor could they be produced in samples plastically deformed at room temperature and then cooled to the temperature of liquid nitrogen.

Briefly, it was demonstrated that this γ to α transformation was promoted by a simultaneous application of plastic deformation and low temperature and could not be produced by these two factors applied separately.

Subsequent and more elaborate experiments established that compositional range, in the family of Fe-Cr-Ni alloys, which responds to the mechanical working at subzero temperatures. Roughly, it can be defined on the triaxial diagram by the following points: 18 pct Cr-4 pct Ni, 12 pct Cr-20 pct Ni, and 30 pct Cr-14 pct Ni.

However, in order to develop this effect to its maximum, these steels have to be thus worked to about 70 pct reduction of the original cross-sectional area. This was demonstrated by rolling and wire-drawing experiments, each performed in several consecutive steps of simultaneous chilling and plastic deformation. Even though this hardening effect can be achieved at temperatures as high as —100°F (—73°C), for practical reasons chilling in liquid nitrogen was found to be more convenient.

Moreover, it also was found that such steels, plastically deformed at a subzero temperature, can be made still harder by aging them at about 750°F (400°C).

Other physical properties are affected in the same proportion as hardness, so that in an 18-8 strip rolled at —300°F (—185°C) and aged at 750°F (400°C) the following values can be obtained: tensile strength, 295,000 psi; yield stress, 290,000 psi; proportional limit, 264,000 psi; elongation, 2.0 pct; reduction of area, 24.8 pct; and hardness, 607 V.P.N. More recently, hardness values of well over 700 V.P.N. have been obtained.

Some preliminary experiments have shown the possibility of a considerable improvement in the wear resistance of austenitic Cr-Ni steels. Likewise, some exploratory tests indicate that the salt-water corrosion resistance of samples thus treated is not greatly affected by the special hardening process described.

In a word, it appears that the phenomenon of martensite formation in austenitic stainless steels, so ably described by Kulin and Cohen, might have valuable practical applications.

S. A. Kulin and **M. Cohen** (authors' reply)—The discussion submitted by Drs. Fisher, Hollomon, and Turnbull is most ingenious, and warrants careful consideration because it points up the very issue that this paper seeks to settle. Of course, it is true that the Boltzmann equation may lead to serious discrepancies at temperatures approaching absolute zero. However, we used the equation only because it is a consequence of the atom-by-atom mechanism of growth which the discussers have postulated, and we wished to test the predictions of this mechanism in a critical way.

In the light of the present paper, Drs. Fisher, Hollomon, and Turnbull suggest that the Boltzmann equation may still be applicable to the martensite transformation for alloys in which the activation energy for growth is larger than the zero-point energy of the lattice (~1000 cal per mol), a possible example being the 0.6 pct C, 6 pct Mn steel of Kurdjumov and Maksimova who reported an activation energy of 1600 cal per mol. However, in the case of the alloys studied in the present investigation, the discussers propose that the activation energy may be less than the zero-point energy and hence the growth may "take on more of the characteristics of sound-wave propagation."

The above distinction appears questionable in view of the following. A 0.6 pct C, 8 pct Mn steel was strained at 4°K, and the martensite content increased from about 90 pct (the amount formed on straight cooling) to about 99 pct during the brief straining period. If the available 10 pct austenite were retained because of a slow atom-by-atom diffusion process, it could not be induced to transform appreciably at 4°K within the few seconds of straining. Furthermore, Kurdjumov and Maksimova[17] have recently reported an activation energy of only 600 cal per mol for a ferrous alloy of 23 pct Ni, 3.4 pct Mn. Notwithstanding this low activation energy, the indications are that the transformation characteristics at low temperatures are quite similar to those of the 0.6 pct C, 6 pct Mn alloy.

These findings indicate that there is considerable doubt concerning the significance of the 1600 and 600 cal per mol values as activation energies for martensitic growth. Other interpretations are possible; for example, Kurdjumov and Maksimova regard these values as the activation energies for nucleation. Thus, the reaction may be controlled by the availability of nuclei rather than by the rate of atomic diffusion. This question will be dealt with by E. S. Machlin in a forthcoming paper on isothermal martensite formation.

Professor Crussard points out some of the difficulties in the athermal embryo theory of martensite nucleation and presents arguments in favor of isothermal nucleation due to the grouping of thermal waves. Actually there is now strong experimental evidence contrary to both of these viewpoints and in favor of the strain embryo concept. The case against isothermal nucleation resulting from thermal fluctuations or waves is indicated by the following experiment conducted by E. S. Machlin. If the isothermal transformation in a 70 pct Fe, 30 pct Ni alloy at −70°C is interrupted by heating briefly to about 60°C, the subsequent transformation at −70°C is almost completely inhibited. On the other hand, if the holding at 60°C is conducted before the first cooling to −70°C, there is no effect on the isothermal transformation at −70°C. In both instances, the thermal fluctuations or waves at −70°C are the same, but the isothermal reaction depends on the state of strain due to the martensite formed on cooling. If relaxation is allowed to take place, the isothermal transformation is reduced in magnitude. In other words, the nucleation of isothermal martensite does not result from thermal vibrations alone, but from their superimposition upon existing strains which are produced, for the most part, by the martensite formed during cooling.

Recent experiments on the effect of plastic deformation substantiate the strain embryo theory of martensite nucleation. Plastic deformation of single crystals raises M_s and slip lines do not stabilize the austenite. The same tendency exists in polycrystalline alloys, but the effect may be obscured because the nonhomogeneous deformation partitions the austenite and causes the martensite to form in smaller units.

The remarkable strengthening of austenitic stainless steel by deformation at subzero temperatures, as described by Drs. Brace and Ziegler, is a striking application of the principles of martensite formation. This unusual type of metal processing has commercial potentialities and its effective utilization will be watched with interest.

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The Isothermal Transformation of a Eutectoid Beryllium Bronze

by Ronald H. Fillnow and David J. Mack

DISCUSSION, A. R. Troiano presiding

R. Haynes *(University of Sheffield, Sheffield, England)*—The authors have presented some interesting data on the isothermal transformations of 6 pct Be-Cu. The reactions are extremely interesting for they appear to show a type of reaction which has not been noted before. The previously accepted temperature of the eutectoid is surprising in view of the relatively rapid rates of transformation observed in these experiments.

The growth of coarse eutectoid from fine eutectoid is an unusual phenomena, since on quenching to room temperature the phases present before and after the reaction appear to be the same. This reaction is attributed to recrystallization of α. Recrystallization usually is associated with the release of strain energy from a deformed lattice. It seems to be unlikely that sufficient strain will be imparted to the lattices of the products of transformation at the high temperatures to provide sufficient energy for a recrystallization process, neither will sufficient energy result from the decrease in interfacial area between the two phases. One would expect that strains will be dissipated almost as soon as they are set up due to the plastic condition of the metal at the high temperature. It is difficult to conceive the recrystallization of one phase affecting the distribution of a second phase with which it is associated.

Consider the formation of a lamellar eutectoid from a solid solution. The conditions may be represented by Fig. 34, the lamellae lying in a direction at right angles to the plane of the paper. The growth of such an aggregate is edgewise, as is expected from theoretical considerations.[19] If we assume that the shaded lamellae are representing the γ phase in copper beryllium and the unshaded the α phase, which are growing through the β

Fig. 34 (left)—Mechanism of growth of eutectoid lamellae.

Figs. 35 (center) and 36 (right)—Hypothetical mechanisms of growth of eutectoid lamellae from finer eutectoid lamellae.

phase, then immediately in front of the advancing lamellae, the beryllium atoms in the β phase would be expected to diffuse towards the γ plates, while copper atoms will tend to diffuse towards the α plates. Consider now the growth of coarse lamellae of α and γ through finer lamellae of α and γ. The conditions are as shown in Figs. 35 and 36. For the coarse lamellae in Fig. 35 to grow, it is necessary that diffusion should occur in the thin lamella of γ phase, or α phase, as the case may be. This implies that in part of the γ lamella some of the beryllium content must diffuse away until formation of the α phase occurs, or in the case of an α lamella, the beryllium content must be increased by diffusion until γ phase is formed in certain areas. Similar difficulties are met in the case of Fig. 36, since diffusion, as indicated, would result in the alloy going from a more stable to a less stable condition. This is contrary to thermodynamics and to previous observations. It might well be asked, where does the constraint which initiates such diffusion come from? On this assumption it may be expected that coarse eutectoid will grow through coarse eutectoid, yet this is not observed. It is suggested, therefore, that at the temperature of reaction the fine eutectoid structure observed is not composed of the α and γ phases but of some intermediate phase, or phases, which break down to α and γ during quenching. Such a phase could give a coarse structure isothermally, while not precluding the possibility of the β phase breaking down directly into the coarse structure. One wonders if there is more in the lamellar appearance of the β phase noted at 500°C than has been assumed. By analogy one is reminded of the formation of eutectoid from both β and β_1 in eutectoid copper aluminum, although the analogy should be treated with caution. Thus two paths seem to be possible for the decomposition, i.e. β to fine eutectoid to coarse eutectoid, and β to coarse eutectoid. It would be interesting to know if after quenching to room temperature the fine eutectoid will continue to form coarse eutectoid when replaced in the isothermal bath.

Klier and Grymko[9] indicated in their paper that the interlamellar spacing of the eutectoid aluminum bronze behaved in an anomalous manner: First decreasing and then increasing as the transformation temperature was lowered. This has been confirmed in a quantitative manner. Do the interlamellar spacings of the fine and coarse eutectoids show a similar behavior?

It would be interesting to learn if any relationship exists between the lamellae of the fine and coarse eutectoids.

It has been observed in eutectoid copper aluminum alloy isothermally transformed to eutectoid below the M_s temperature that pseudomorphs of the martensitic structure can be seen, so that pseudomorphs of the fine eutectoid in the coarse eutectoid do not seem to be evidence for the phases present in the fine eutectoid being α and γ.

At the lower temperatures it has been observed that a metastable precipitate forms early in the reaction and then quickly disappears and is followed by the "ripple" structure. The product of such a reaction cannot be β. Would it not be better to designate it by β' or some other symbol? The ripple structure then takes on a mottled appearance. This is similar in appearance to the latter stage of the β to β_1 reaction in eutectoid copper aluminum. May not the reaction be analogous?

There seems to be little justification for the use of two hardness scales on the hardness-transformation-time diagrams. Even in a single phase alloy the results are not directly comparable. On a multiphase alloy one wonders if any simple correlation can exist. The use of microhardness for following isothermal reactions seems to be open to question. Such a method must result in the hardness of only one of the many constituents being determined by any one impression, with the result that for a number of impressions which are randomly distributed the hardness of a partially transformed specimen will vary over a very wide range. This difficulty can be overcome by the use of a large indentor, say a 10 mm Brinell ball: This is not possible if small specimens are to be used, or by taking numerous hardness impressions and computing a mean value. The claim that the microhardness data correlates well with observed microstructures seems rather sweeping. In Fig. 30, for example, the results appear to show a scatter of 100 points pyramid for a structure which does not change greatly with time. Fig. 19 shows a number of undulations in the curve. On examination of the curve it might be concluded that points (3) and (4) (my reference marks in Fig. 37) were of significance. This is not so. It is possible to draw a fairly smooth curve, as shown, for the results from 500°C downwards. This, however, results in the elimination of the "significant" change in direction at (2). To a lesser extent this criticism can be levelled at most of the hardness curves. One concludes that the use of microhardness, by itself, is completely unsuitable for following the reactions, and that the various "start" and "finish" times on the curves are derived from microscopical evidence.

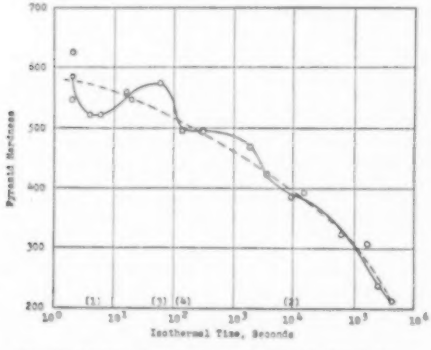

Fig. 37 (right)—Authors' Fig. 19 plus additional data.

Confirmation of the microscopical results is made by the X-ray diffraction method. By examination of the photographs in the cases of coarse and fine eutectoid, it can be seen that at high angles of reflection the doublet x of the K_α radiation appears to be resolved, while in the case of the slowly cooled alloy the ring is blurred. In a quenched alloy the rings are expected to be blurred and the doublets unresolved at high angles. This is borne out by quenched specimens of the eutectoid Cu-Al alloy. One is led to wonder how efficient was the quench, or if the specimens have received a stress relieving anneal? If so, it is not possible that changes may have occurred.

J. E. DeMoss (*University of Notre Dame, Notre Dame, Ind.*)—I have been working on the transformations of the β phase in the Be-Cu system for some time and, hence, particularly appreciate the peculiarities and complexities which confronted the authors.

From my results, I agree with the authors that the accepted eutectoid horizontal temperature is too low and that actually it is somewhat above 600°C. This has been pointed out by Thomas.[11]

My results on the isothermal transformation of a eutectoid Be-Cu alloy are in essential agreement with those of the authors. I have observed many of the

"unusual microstructures" which have been shown in this paper including the initial appearance of fine pearlite and its ultimate replacement by coarse pearlite. However, I find it difficult to accept that the coarse pearlite forms from the fine pearlite by a nucleation and growth process, although that may appear to be the mechanism.

Evidently the β grain size of the authors' alloy must have been reasonably small. I have observed that the time for completion of the isothermal reaction is quite long, even at 500°C, when the β grain size is of the order of 1.5 mm average grain diameter. The time for the beginning of the reaction, though, seems affected very little by the β grain size. The writer has found that it is possible to refine the β grain size only by cold working the slowly cooled alloy after it has transformed to α plus γ and reheating to the β-phase field. Heating through the allotropic transformation, as in steel, seems to have no effect on the β grain size. Do the authors have any information on this point?

I cannot agree with the authors' statement in point 5 of the summary that "Even though the cooling of the specimen is interrupted by an isothermal holding at an intermediate temperature, the remaining beta can also be retained at room temperature by the subsequent quench." I have isothermally transformed a eutectoid specimen at 300°C for 1 hr and obtained no microscopic evidence of transformation. The specimen appeared to be all β, yet the X-ray diffraction pattern showed only α and γ lines and no β. I also have obtained X-ray evidence that a quenched eutectoid β undergoes transformation on remaining at room temperature. I can cite many more very interesting and confusing X-ray results on this alloy, but my point is that the transformations of the β phase in the Be-Cu system are far from simple, and that what appears to be β may not always be β.

J. T. Richards (*Beryllium Corp., Reading, Pa.*)—The authors of this excellent work have identified three isothermal transformation products: Fine pearlite, coarse pearlite, and β. There is no indication, however, as to the structure in which the microhardness determination was made. It would have been of interest if microhardness curves had been plotted for each structure at the transformation temperatures producing more than one structure.

Although Raynor[12] has given the eutectoid temperature as 575°C based on four prior investigations, there is considerable evidence to substantiate the authors' claim that this value is too low. Masing and Dahl[13] found by microscopic investigation that a 6 pct Be-containing alloy was still homogeneous after quenching from 620°C, although there are indications of incipient decomposition. On the basis of microscopic and hardness tests by Ewing,[14] the eutectoid temperature falls between 600° and 620°C. Borchers and Otto[15] claim that the eutectoid temperature may run as high as 50°C over the generally accepted figure (575°C), based on a dilatometric investigation with a maximum heating rate of 0.65°C per min.

Perhaps one of the most complete studies of the eutectoid transformation was conducted by Thomas.[16] From dilatometric investigations, an average of 620°C was obtained on heating at 0.5 to 1.0°C per min, while cooling at 1°C per min gave 601°C. Electrical resistance measurements on heating yielded 618°C. These results were checked by thermal analysis and values of 618°C (on heating at 4°C per min) and 601°C (on cooling at 5°C per min) were obtained. Thomas claims that the low values previously reported result from dilatometric curves being taken only for decreasing temperatures and at too rapid cooling rates.

In considering the above results together with those of the present authors (608°C), a range of 608° to 610°C is suggested for the eutectoid temperature instead of the accepted figure of 575°C.

There is good agreement on the hardness of the various structures between Ewing[14] and the present paper. For specimens quenched from 700° to 800°C,

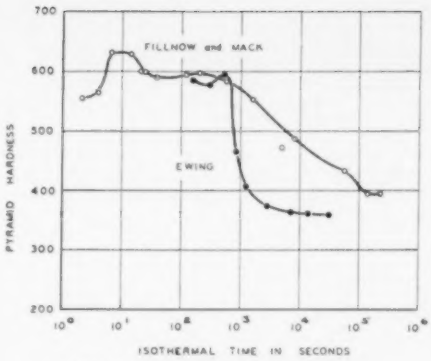

Fig. 38—Changes in hardness at 400°C.

Ewing obtained Vickers hardnesses ranging from 561 to 614 for the β phase, while the present authors give values from approximately 550 to 640. Ewing reports a hardness of 243 for a specimen heated at 570°C for 2½ hr, comparing with an approximate value of 245 in the present paper for the same time at an isothermal transformation at 550°C. As a matter of interest, Ewing found that the hardness of 243 obtained by heating for 2½ hr at 570°C increased to 566 upon further heating for 15 min at 620°C.

Although Ewing did not employ isothermal heating, his results obtained by quenching to room temperature followed by reheating give the same general trend. Fig. 38 superimposes one of Ewing's curves on the authors' Fig. 23.

R. H. Fillnow and **D. J. Mack** (authors' reply)—The writers wish to thank Messrs. Haynes, De Moss, and Richards for the additional information they have contributed. All results indicate that the currently accepted eutectoid temperature must be revised upwards to about 610°C.

The authors have repeatedly observed what Professor De Moss points out, i.e., that the β grain size in this alloy cannot be refined by simple heating through the transformation range, as is the case with steel. This phenomenon is well known in aluminum bronzes and is apparently the customary behavior in eutectoid transformations where neither component exhibits allotropy. Thus there are two types of eutectoid transformation as Harrington[17] has pointed out: The allotropic eutectoid and the plain eutectoid.

Unfortunately, the authors' X-ray diffraction studies were confined to the lamellar α plus γ aggregates and hence we cannot comment on Professor De Moss' results regarding the transformation of β to α and γ without change in microstructure. Such a transformation is certainly possible and may be associated with some of the transitory changes in microstructure that occur. We are in complete agreement with Professor De Moss concerning the complexity of the transformations in this system.

Professor Haynes has pointed out the objections to the simple mechanism proposed by the authors for the two pearlite reactions. The possibility of the fine pearlite being composed of metastable phases, say α' and γ', should not be ruled out until more definitive experiments have been performed. However, one need not rule out recrystallization of the α because of strain energy requirements and the apparently logical assumption that at high temperatures this strain energy would be released by localized plastic flow for the following reasons:

1—"Recrystallization" of α in an alloy containing 1.92 pct Be has been observed at 400°C.[8] Here the mechanism is a solution and redeposition of the precipitate at the advancing interface. The appearance

of the coarse pearlite suggests this mechanism of discontinuous precipitation.

2—Release of the strain energy might not be possible because of the rigidity of the lattice caused by its high solute metal content and the restraint imposed on the α by the adjacent lamellae of γ. As a matter of fact, experiments now underway on the Cu-Sb eutectoid have shown that a quench of the high temperature body-centered tetragonal β phase into a salt bath held only 20° below the eutectoid temperature (436°) results in strain markings due to anisotropic contraction of the tetragonal phase. These strain markings later serve as sites for the precipitation of the stable end product phases.

It is believed that the apparently diverse views of Professor Haynes and the writers will coincide if the existence of metastable α' and γ' or some transition lattice can be established, because there will then be an easy energy path for the reaction to follow.

No quantitative measurements have been made on the lamellae of either the coarse or fine pearlite. Both get finer as the transformation temperature is lowered, but no coarsening was observed below the nose of the transformation curves.

In answer to Professor Haynes' objection to the use of microhardness methods, the authors found that a very light load was necessary for obtaining hardness values of the retained β. With the heavier loads used, for example, with a Rockwell C scale, the indenter had a tendency to shatter the brittle β. For the sake of uniformity of data, microhardness determinations were used throughout.

The authors must remind Professor Haynes that microhardness determinations were not used to follow the isothermal reactions. Any start or finish times, as given on the various hardness curves, were obtained solely through metallographic methods. Hardness data was obtained only for purposes of a qualitative correlation with metallographic data. Since this was the purpose of the hardness readings, several traverses were made across the specimen if two phases existed, and a mean value taken. In answer to Mr. Richards, this gave a very acceptable, reproducible hardness value. The variation in hardness values, shown on Fig. 30, was the largest spread found throughout the work. Approximately 90 pct of the hardness values obtained by the traverse method had a spread of only 10 or 20 points on the Vickers scale. The Rockwell scale was placed on the hardness plots in addition to the Vickers hardness scale only as a guide for those readers unfamiliar with the Vickers hardness numbers.

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The Effect of Alloying Elements on the Plastic Properties of Aluminum Alloys

by J. E. Dorn, P. Pietrokowsky, and T. E. Tietz

DISCUSSION, R. M. Parke presiding

A. I. Snow *(University of Chicago, Chicago)*—In a footnote to their paper the authors cite the work of Ageev and Guseva on the distribution of the electronic density in aluminum and quote from *Chemical Abstracts* that: "Comparison between the experimental (structure factor) curves and the theoretical curves drawn for Al^{+} and Al^{+++} leads to the conclusion that in the metal crystal lattice, Al is present as approximately bivalent ions." The words in parentheses, "structure factor", which are evidently inserted by Dorn and coauthors, are misleading since what was compared were not structure factor curves but electron density curves, namely, the ones obtained by using the structure factors as coefficients in a three dimensional Fourier series compared with electron densities calculated for various assumed valence states. In a later paper Ageev and Ageeva use intensity data obtained by themselves, instead of from the literature as in the first paper, and this time arrive at a valence for metallic aluminum of approximately 2.5. The results of both papers by Ageev and coauthors concerning the valence of aluminum are open to serious question since it has been shown theoretically[18] that no matter whether aluminum is mono-, di- or trivalent the atomic scattering factor curves in the range of observable X-ray diffraction maxima are identical. These atomic scattering factor curves only differ appreciably below the value of $\sin\theta/\lambda$ of the first reflection that it is possible to observe (111). Therefore the structure factors and intensities of a given reflection will be identical for all three possible valence states and the use of the experimentally determined structure factors will lead to no knowledge of the valence states of aluminum no matter how mathematically manipulated. There are other serious objections to the treatment of the experimental data by Ageev and coauthors in these and other papers which I intend to discuss elsewhere.

J. E. Dorn, P. Pietrokowsky, and **T. E. Tietz** (authors' reply)—We wish to thank Dr. Snow for his interpretation of the results obtained by Ageev and Guseva on the electron density curves in metallic aluminum. They are looking forward with interest to Dr. Snow's paper on this subject.

[18] R. W. James: *The Optical Principles of the Diffraction of X-rays.* p. 303. (1948) London. G. Bell and Sons, Ltd. James points out the difficulty in obtaining the valence of aluminum by comparison of calculated and experimentally obtained atomic scattering factor curves but does not point out that this must also necessarily entail difficulty in obtaining valence values from electron density curves.

The Properties of Some Magnesium-Lithium Alloys Containing Aluminum and Zinc

by Robert S. Busk, Donald L. Leman, and John J. Casey

DISCUSSION, R. M. Parke presiding

P. D. Frost *(Battelle Memorial Institute, Columbus, Ohio)*—I would like to comment on the statement on p. 946 of the paper, in which the authors say that increasing lithium increases stability. This is somewhat misleading. Refer, for example, to the 6 pct Al alloy in Table III. Increasing the lithium from 3 to 12.5 pct results in a high strength alloy. This alloy attains its maximum yield strength in the quenched condition; subsequent aging at 180°F effects softening. When the lithium content is increased to 16 pct, an alloy is produced which has lower strength as quenched, but whose aging cycle at 180°F is somewhat slower than that of the Mg-12.5 pct Li-6 pct Al alloy. Thus, this alloy undoubtedly attains its maximum strength after aging a few hours at 180°F.

If aging were carried out for a much longer period

than 16 hr, it would be observed that the final strength, for a given aluminum content, would be higher as the lithium was decreased. This is demonstrated for an 8 pct Al alloy in Fig. 4. The alloy having 13.1 pct Li attains maximum hardness as quenched from 700°F. Increasing the lithium to 15.3 pct delays the aging cycle slightly, and the peak hardness occurs after about 1 hr at 200°F. The stability, however, is actually lowered.

When the lithium level is lowered to 8.8 pct, the hardness, as quenched, is lower. However, the aging curve is considerably flatter, and the hardness after 1000 hr at 200°F is higher than either of the higher lithium alloys.

D. L. Leman (authors' reply)—Mr. Frost's data on the extended aging of Mg-Li-Al alloys is an important contribution to this paper and is appreciated. However, it was not our contention that increasing lithium increases stability of properties over the entire range of lithium studied. This statement was made on the basis of alloys containing 12 and 16 pct Li, both of which have a wholly cubic structure. The exceptional high strength properties obtained in this alloy system are possible only with the predominately cubic alloys. The subsequent major loss of strength is associated with the high strengths produced. Alloys which have a predominately hexagonal crystal structure are definitely more stable than the cubic alloys but at a lower strength level as shown in Table III.

We also believe that the statement regarding the

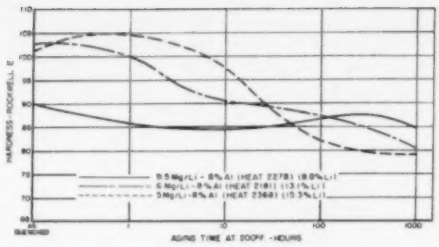

Fig. 4—Effect of lithium on aging Mg-Li-Al alloys.

effect of lithium content on property stability is applicable. High strength is produced by precipitation hardening and the question of stability is therefore dependent on the tendency of the alloy to overage rather than on its strength in the overaged condition. It is not uncommon for the strengths of age-hardenable alloys in other systems to equalize in the overaged condition even though the aging curves may differ considerably. The superiority of Mg-16 pct Li-10 pct Al over Mg-12.5 pct Li-10 pct Al (or Mg-15.3 pct Li-8 pct Al over Mg-13.1 pct Li-8 pct Al) in this respect is significant and would be expected to be even greater as the temperature of exposure is lowered.

The Effect of Sodium Contamination on Magnesium-Lithium Base Alloys

by P. D. Frost, J. H. Jackson, A. C. Loonam, and C. H. Lorig

DISCUSSION, R. M. Parke presiding

R. J. M. Payne and **J. D. L. Eynon** *(J. Stone and Co. Ltd., Deptford, London, England)*—We at Deptford have worked on Mg-Li alloys since May 1947. It is hoped that a formal paper which will be largely concerned with the effects of impurities will be presented to the Institute of Metals (London) in the near future. Pending its publication we offer the following comments on this paper.

As the authors observe, the preparation of satisfactory Mg-Li alloys is largely a matter of securing freedom to a sufficient degree from the other alkali metals which are so often found in association with the basic metals. We too started with the LiCl-KCl flux and impure lithium, we changed to fluxes composed wholly of lithium salts, we refined our lithium by vacuum fusion until such time as the high grade lithium became available, we grew more watchful for impurities and became increasingly critical of our raw materials (including the magnesium) as the work proceeded. In our investigations we were greatly handicapped by the lack of reliable analyses, and it is only recently, and as a result of much careful work, that methods for determining the very small amounts of sodium and potassium, which we now know to be significant in alloys, have become available. Investigations carried out at the Admiralty Materials Laboratory, Holton Heath, Dorset, England, have put analytical procedures on a firm footing and we feel that we can now speak with confidence regarding the amounts of alkali metals which can be tolerated in the final alloys: We can also give tolerance limits for impurities in basic metals and salts. We agree that the principal difficulty in working with Mg-Li alloys is with sodium. As we see it, the main concern of the present authors has been to secure the full ductility of the material in the cast or wrought condition and to this end they have found it advantageous to reduce sodium contents to a low level. We have discovered a further reason for excluding sodium from melts of Mg-Li alloy and one which necessitates that the amount of this element be held at an even lower level. We have found that while alloys containing about 0.01 pct Na may in the cast condition show the full ductility of which the material is capable, such alloys may be unstable and liable to develop intergranular weakness due to the precipitation of sodium. We have evidence that there is a very marked difference in the solubility of sodium in the β phase between temperatures of about 400°C and room temperature, and that alloys which were ductile as-chill-cast or as-wrought may embrittle very seriously on mild heating or even on standing at room temperature. To avoid these effects we consider it desirable to limit sodium to much smaller contents than those which just permit good elongation to be obtained in the cast or wrought state. The degree to which complex alloys are affected by sodium depends on the particular elements added to the basic Mg-Li alloy. From our own work we have seen that the sensitivity to sodium is considerably less marked in wrought than in cast alloys, and it may be for this reason that Frost and his colleagues have found as much as 0.03 pct Na unobjectionable in an alloy containing 9 pct Li and 4 pct Zn (Fig. 1): It is possible under certain conditions of heat treatment that this same alloy would have developed intergranular weakness through the precipitation of sodium. A difference in the sensitivity to sodium as between wrought and cast products would be understandable in view of differences in grain size: For an alloy of given sodium content, the concentration of sodium at the boundaries will obviously be less in the case of a fine grained material due to the greater area over which the impurity is spread. A tendency for sodium to seek grain boundaries has already been reported by Busk, Leman, and Casey.[1] These authors, however, refer specifically to ternary Mg-Li-Al and Mg-Li-Zn alloys and have not apparently realized that the same phenomena may be met in basic binary compositions. So far we have seen no report of solubility varying with temperature. We have made a conclusive demonstration of the solubility of sodium by heating to 400°C and quenching an alloy containing sufficient sodium as to cause it to break with zero elongation when tested as chill cast: The specimen thus heat treated was quite ductile.

We have spent much time, as have the American workers, in seeking methods of eliminating sodium

from melts, thus removing the need for very high purity in basic materials; success in this field has, however, been limited. We do not propose to pursue this topic at any length, but will record that we do not find the LiCl-LiF flux to have outstanding virtues as regards sodium removal; in fact we regard it as inferior to simple LiCl in this respect. We are aware that the chloride-fluoride flux has other advantages which make it preferable to the simple chloride in certain circumstances.

H. M. Skelly *(Aluminum Laboratories Ltd., Kingston, Ont., Canada)*—Have any tests been made for flux inclusions in melts of Mg-Li alloys prepared under a covering flux of 75 pct LiCl plus 25 pct LiF?

P. D. Frost, J. H. Jackson, A. C. Loonam, and **C. H. Lorig** (authors' reply)—It was a pleasure to receive the excellent discussion from Messrs. Payne and Eynon. The observation regarding the difference in solubility of sodium between 400° and 20°C is very interesting and may account for some of the hardness changes we have obtained in aging quenched binary alloys.

Most of our work has been with wrought alloys. It has been our experience that cast Mg-Li ingots must be hot worked considerably to develop good properties. The precipitation of sodium at the boundaries of coarse grains undoubtedly contributes to low ductility in castings. Of course, a wrought, fine grained structure usually has greater ductility than a cast structure, even in the absence of contaminating elements.

It is noteworthy that Messrs. Payne and Eynon found that LiCl removed sodium more effectively than the LiCl-LiF flux. We found that the LiCl-LiF flux was very effective. However, we believe that the efficiency of these various salt mixtures depends to a major extent on the sodium content of the salt as procured.

In reply to Dr. Skelly, fracture tests on cast ingots and wrought specimens rarely reveal flux inclusions in Mg-Li alloys. On the other hand, the alloys often become badly pitted under humid conditions. We are, at the present time, attempting to evaluate the effect of contaminating materials, such as flux, on corrosion resistance.

Hydrogen Embrittlement of SAE 1020 Steel

by J. B. Seabrook, N. J. Grant, and Dennis Corney

DISCUSSION, R. M. Parke presiding

G. A. Moore *(University of Pennsylvania, Pittsburgh)*—The authors are to be congratulated for making several very important additions to our information on the nature of hydrogen embrittlement. While it is pleasing that the relation of ductility to hydrogen content has been so closely checked with our previous work,[1] the agreement is perhaps more fortuitous than realized, since steels of quite different carbon content and structure are compared. The agreement emphasizes that the embrittling effect is mainly on the ferrite phase, while cases of disagreement, such as the occurrence of "permanent damage," re-emphasize the fact that hydrogen tends to be highly segregated, so that its effects must be more localized (microscopically) in the cast material than in these electrolytically charged cases. The hydrogen content to cause actual microcracks and thus decrease impact values, therefore, varies widely with structure and source of hydrogen.

A great advance has been made by the inclusion of the natural stress-strain data in the present paper. At the time of the earlier report, we did not realize the fallacy of using the metallurgically meaningless engineering values until too late to obtain the complete data, an omission which I have personally had numerous occasions to regret. Approximate determinations of the fracture stress did show a better correlation to hydrogen than the ductility measurements, but the lack of the stress-strain curves prevented a complete analysis of the effects occurring. The authors would be justified in discussing Fig. 5 in much greater length. The figure appears to justify analysis as follows:

The conclusion of Smith[4] that none of the hydrogen is in actual solution in the lattice is supported by the lack of hydrogen effect on the yield strength and hardness. The conclusion that after slight strain the hydrogen is occluded in rifts, mosaic disjunctions, or the tension sides of Taylor dislocations, and spreads these openings, is supported by the fact that the effect on the flow curve could be expressed as the addition, without dimensional change, of a plastic strain of 0.05 to 0.10, in line with earlier statements that "the effect of hydrogen is similar to that of a little cold working." This mode of occlusion is realized to induce tensile microstresses, largely triaxial, in the noninterrupted portions of the lattice structure, which stresses tend to interfere with flow. These stresses now may be estimated for the first time from the information that the flow stress of charged bars lies about 6000 psi above that of uncharged bars. Presuming the actual value of the critical shear stress unaffected by hydrogen, then in the presence of a radial biaxial tension, either the maximum or octahedral shear stress laws require that the applied tensile stress be increased by the same amount to maintain flow. Thus the microstresses induced by the hydrogen here have a net unbalanced radial component averaging about 6000 psi, except at the immediate surface where they are noted to have been relieved by blistering. The unknown triaxial component in the axial direction, which balances out in testing, may be added to obtain the actual microstress, but since the observed flow stress does not increase with further addition of hydrogen after about 2 ppm (or 0.2 relative volume), it is unlikely that the stresses ever actually exceed 10 pct of the estimated 100,000 psi calculated on the assumption that the volume occupied by the precipitated hydrogen is negligible.

The old argument as to whether the embrittlement is due directly to the presence of the rifts, or to the microstresses around the rifts, therefore appears resolved. The fracture stress is lowered progressively by continuing increases of hydrogen content, with an observed loss of 40,000 psi at contents of 5 to 10 ppm. The idea that the actual strength of the metal remains constant and the 40,000 psi stress is supplied by the gas pressure is incompatible with the small and fixed effect on the flow stress, hence it is clear that only a minor portion of the embrittling action is due to the stress, while a major portion is due to the extension of the rift system, with its interruption of the coherency of the metal and obvious notch effects.

As this analysis is of necessity based on the published figure alone, perhaps the authors will be so kind as to check it against the unpublished data and investigate other interesting details. For example, it appears that hydrogen reduces the amount of uniform strain just enough that the stress at maximum load is not changed, which may help explain how the hardness can be unchanged while the tensile strength rises, and perhaps also why some observers find hydrogen to lower the tensile strength, some to raise it, and many to find it to have no effect. Certainly the publication of more natural stress-strain data in connection with hydrogen embrittlement problems will be a very important addition to our understanding of the mechanism involved.

J. B. Seabrook, N. J. Grant, and **D. Carney** (authors' reply)—The authors thank Dr. Moore for his discussion and interesting analysis. It may turn out that the agreement as to minimum hydrogen required for maximum embrittlement is fortuitous. If the embrittling effect is truly mainly in the ferrite phase, however, it is conceivable that further experiments with the embrittlement of ferritic material will show agreement with the figure of 5 ppm at maximum embrittlement for the hot-rolled condition.

Because hydrogen segregates at the grain boundaries and interdendritic zones, it is expected that hydrogen will be much more segregated in cast materials, resulting in permanent damage. Accordingly, low values of hydrogen in a cast material need not signify freedom from damage, especially if the hydrogen has had an opportunity to diffuse out.

We hesitate to make specific far-reaching conclusions regarding all the information to be derived from the true tensile strength curves. We are not sure that one can express the differences in the flow curves as differences in strain; the effect may rather be looked upon as an increase in flow stress due to the occlusion of hydrogen shortly before the increase is measured. In this respect the effect of hydrogen would definitely not be "similar to a little cold work."

We agree that the difference in fracture stress of 40,000 psi is not supplied by gas pressure. High pressures can, however, be exerted. The surface bursts which occur when more than about 6 ppm of hydrogen is charged indicate the tensile strength of the cold-worked (from machining) steel surface is exceeded.

As much a reappraisal of all the data as time would permit has not disclosed sufficient evidence to extend our analysis except for one factor. It should be emphasized that the division of high and low curve samples was on a general basis, and no definite curve of increased flow stress vs. hydrogen content was obtained with the accuracy of our experiments. Likewise, the proposition that stress at maximum load is not changed cannot be supported by our data. However, for the slow strain rate specimens, the strain at maximum load was noticeably less than for the usual rate tests. Perhaps some hardness reading change would be noted in hydrogen-charged specimens if the hardness tests were performed at a slow rate of application of load.

P. Bastien and **P. Azou** *(Ecole Centrale des Arts-et-Manufactures: Laboratorie de Physique des Métaux, Paris, France)*—We think that the measurement of the volume of hydrogen extracted under mercury from steel specimens (previously treated with this gas by pickling or electrolytic action) by degassing at room temperature does not lead to systematic errors when the usual precautions required for mercury handling are taken. Some air can be entrained by specimens when put in mercury, but tests made by one of us indicate that the collected gas contains at least 99 pct hydrogen. Hydrogen concentration in pickled or electrolytically treated specimens is more heterogeneous than in specimens as received from the steel mill. In the first case, it is particularly high at or close to the metal surface. Therefore, we think that degassing by heating in vacuo may be inadequate, for a great part of the hydrogen may be expected to be lost due to the reduced pressure prior to the actual measurements. We should appreciate hearing some details of the degassing practice used by the authors.

Hydrogen collected under mercury at room temperature is the easily diffusing gas which causes embrittlement of pickled or electrolytically treated specimens. One of us has given evidence that a relation exists between the volume of the easily diffusing hydrogen and the brittleness of the metal.[14]

We are particularly interested in the results obtained by the authors with true stress-true strain tensile tests. We also have plotted true tensile curves for an annealed 0.15 pct C steel both with and without hydrogen. The main results have been presented[15] at

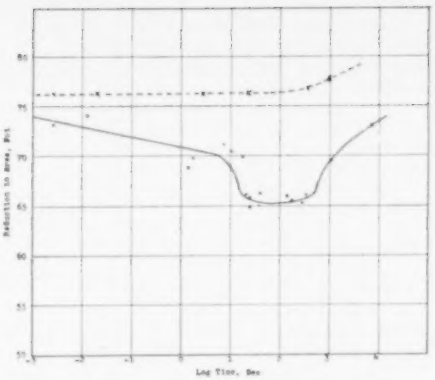

Fig. 9—Effect of strain velocity on reduction of area.

Lower curve shows the effect of hydrogen treatment on the reduction of area of the untreated steel in the upper curve at various rates of straining.

the French Academy of Sciences on April 4 and May 9, 1949. The conclusions reached by the authors are in good agreement with ours. Hydrogen influences only the true rupture stress. The true tensile curves are superimposable whether the steel contains hydrogen or not, but the fracture will occur at a lower true stress when there is hydrogen in the steel; a fact in agreement with a smaller reduction in area. Moreover we have shown that when the testing temperature decreases, the true breaking stress is lowered for a pickled steel. This fracture is semibrittle for ordinary and brittle for hydrogen-bearing steels; the phrases "semibrittle" and "brittle" being used in accordance with Shevandin's work.

In addition we have shown that: 1—Iron and steel brittleness due to hydrogen disappears below −110°C and reappears reversibly by heating above this temperature.[16] 2—The influence of the gas on the elastic modulus and damping capacity will be smaller if the test used to determine the property being studied causes smaller elastic deformation and apparently is reduced with increasing elastic strain during the test.[17] 3—In tensile tests at room temperature with the duration of the test ranging from 1/150 sec to 2 hr 20 min, hydrogen has no effect on the capacity for deformation at high speeds, its effect becoming a maximum for times between 10 sec and 30 min, then becoming gradually smaller with low rates of straining[18] as shown in Fig. 9.

Our views agree with the authors that hydrogen in the proton condition in the iron lattice[19] has, within the elastic range, no effect on the properties of the metal. Under plastic deformation, the hydrogen, probably diffusing through the motion of dislocations, will collect at the volumetric defects at various locations in the metal where, when it can recombine as molecular hydrogen, it will develop triaxial forces which resist deformation by slip and cause hydrogen embrittlement. Since segregation requires diffusion, it will not occur at the lowest temperatures; below −110°C for our tests, where thermal agitation is too small, nor with high rates of plastic straining when the time is too short for mass displacement of protonic hydrogen.

This is the reason why hydrogen does not alter significantly the impact resistance of steels, which we have measured over a temperature range from −70° to 18°C using standard type specimens. Similarly it is not surprising that there is no difference in the hardness of test pieces of the same steel with and without hydrogen. In hardness testing, the rate of straining is very high and the plastic deformation is

completed before the time required for hydrogen segregation and resultant action.

J. B. Seabrook, N. J. Grant, and **D. Carney**—We are particularly pleased to find our results in such good agreement with the results of Messrs. Bastien and Azou. Our experience with degassing under mercury has not been too satisfactory. Frequently we found large disagreement between values so obtained and those obtained by vacuum fusion in an iron-tin bath. Regarding the degassing techniques used in this work, Messrs. Bastien and Azou are referred to the two papers by Carney, Chipman and Grant, refs. 11 and 12 of the paper. In this connection we believe that the method described in the above papers is by far the most accurate, reliable, rapid, and simple method presently available for hydrogen analysis.

It is difficult to conceive that the so-called "easily diffusing hydrogen" is anything other than the hydrogen which occupies the outer position of the specimen.

The absence of a hardness effect in view of the rapid rate of straining during the test would certainly be a feasible explanation as suggested by Messrs. Bastien and Azou.

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[11] P. Bastien: *Rev. de Métallurgie* (1940) **37**, pp. 225-237, 272-284.

[12] P. Bastien and P. Azou: *Comptes Rendus* Académie des Sciences (1949) **228**, pp. 1337-1339, 1651-1653.

[13] P. Bastien and P. Azou: *Comptes Rendus* Académie des Sciences (Sept. 5, 1949) **229**, pp. 549-551.

[14] P. Bastien and P. Azou: *Comptes Rendus* Académie des Sciences (July 10, 1950) **231**, pp. 147-148.

[15] P. Bastien and P. Azou: Académie des Sciences (Dec. 15, 1950).

[16] E. Darmois: *Journal de Physique et du Radium* (1950) **11**, pp. 577-582.

Aging Characteristics of Magnesium-Lithium Base Alloys

by P. D. Frost, J. G. Kura, and L. W. Eastwood

DISCUSSION, R. M. Parke presiding

D. L. Leman *(Dow Chemical Co., Midland, Mich.)*—The presentation of this paper is indicative of the continued interest in the high strength properties of some of the ultra-light Mg-Li base alloys. The general observations on the problems of property instability and lack of ductility in the high strength alloys is in close agreement with the results of work done at The Dow Chemical Co.[1]

The authors mention that the alloy 9.5 Mg/Li-7 pct Al-3 pct Sn may have resistance to stress-corrosion cracking nearly equal to that of AZ31A-H24.* Using a different testing method, we find it to be appreciably less resistant. The stress-time curves for bars spring-loaded in simple tension and exposed up to four years in a rural atmosphere are given in Fig. 13. Although the time before failure occurring at a given stress-level varies considerably for AZ31A-H24, the failures for 9.5 Mg/Li-7 pct Al-3 pct Sn all took place within such a short time that no significant variation would be expected on more extensive testing. The difference between the two alloys would not be readily apparent at stresses as high as those reported in the paper, because failures occur in both alloys in a comparatively short time. For details of the testing method used and other factors affecting stress-corrosion testing see Loose and Barbian.[2]

We have also tested the creep characteristics of 9.5 Mg/Li-7 pct Al-3 pct Sn at 95°F. The sustained-stress which will produce 0.1 pct extension in 100 hr is 15,000 psi as compared to 18,000 psi for AZ31A-H24.

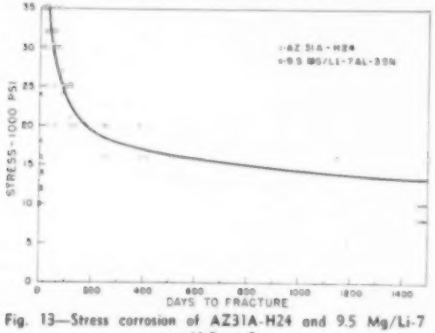

Fig. 13—Stress corrosion of AZ31A-H24 and 9.5 Mg/Li-7 pct Al-3 pct Sn.

It may be well to mention our conclusions at The Dow Chemical Co. based on the extensive investigation of Mg-Li base alloys. Without going into detail on specific compositions it can be said that there are three distinct classes of alloys as follows:

1—Soft ductile alloys which have a cubic or predominately cubic crystal structure. These are outstanding with respect to formability and toughness at a tensile and compressive yield strength level of 20,000 to 25,000 psi.

2—High strength alloys which have a cubic or predominately cubic crystal structure. These compositions may also be of the Class 1 type in the soft condition but their strength can be trippled by precipitation of the $MgLi_2X$ phase.

3—Intermediate strength alloys which have an hexagonal or predominately hexagonal crystal structure. Maximum strength in these is developed by cold working or the combination of heat treating, cold working, and aging. The typical tensile and compressive yield strength level is 40,000 to 45,000 psi.

Many of the compositions studied possess interesting properties in one respect or another, but none as yet have been found to have a suitable combination of mechanical properties, secondary properties, and service characteristics which would warrant acceptance as a commercial product. In particular the soft ductile alloys have poor creep resistance, the high strength alloys soften on continued exposure at slightly elevated temperatures and in general are quite brittle in the strong condition, and the intermediate strength alloys are characterized by low notch toughness and high stress-corrosion sensitivity.

The approach to the development of a usable alloy of maximum strength must be through a fundamental study of the mechanism of $MgLi_2X$ hardening. Creep, toughness, stress corrosion, and possibly other secondary properties should be studied on the basis of alloy design.

P. D. Frost, J. G. Kura, and **L. W. Eastwood** (authors' reply)—Mr. Leman's contribution to this paper is greatly appreciated. It is assumed that the stress corrosion and creep tests to which he refers were con-

* AZ31A-H24 is the newly accepted ASTM designation for AZ31X-h.

[1] R. S. Busk, D. L. Leman, and J. J. Casey: The Properties of Some Magnesium-Lithium Base Alloys Containing Aluminum and Zinc. Trans. AIME (1950) **188**, p. 945; Journal of Metals (July 1950).

[2] W. S. Loose and H. A. Barbian: Stress Corrosion Testing of Magnesium Alloys. Symposium on Stress Corrosion Cracking. ASTM-AIME (1945).

ducted on sheet specimens of the 9.5 Mg/Li-7 pct Al-3 pct Sn alloy prepared at Battelle and sent to Dow for this purpose.

It is difficult to correlate stress-corrosion data obtained by two different methods of testing, particularly where so few specimens are involved. The objections to the bending method of loading are recognized. However, these do not offset the usefulness of this type of test, particularly for materials, such as the 9.5 Mg/Li-7 pct Al-3 pct Sn alloy, whose compressive and tensile yield strengths are equal.

Although the Dow and Battelle results are in fair agreement for the highly stressed specimens, the discrepancy between the results for the lower stressed specimens must await further tests for clarification.

We do not have creep data for the 9.5 Mg/Li-7 pct Al-3 pct Sn alloy. However, we are evaluating the creep and stress-rupture characteristics of 9.5 Mg/Li-7 pct Al-1 pct Sn alloy sheet. Under a stress of 30,000 psi, one specimen failed after 58½ hr. Under a stress of 20,000 psi, one specimen has elongated a total of 0.4 pct in 100 hr, including the initial deformation. It is assumed that the Dow values represent total elongation in 100 hr, and not creep rate.

The following additional remarks concerning the corrosion resistance of Mg-Li base alloys may be of interest. Panels of several alloys have been exposed to the semitropical marine atmosphere at Daytona Beach, Fla., since June 7, 1950. The corrosion rates obtained to date for these alloys are given in Table VIII.

One of the authors carries a pocket piece of an alloy containing 87 pct Mg-9 pct Li-4 pct Zn. This specimen lay on the author's desk in New York City for four years, and for one year has been in contact with pocket keys and other metallic objects. Most of the surface has acquired a thin, dark, protective layer, while the edges remain bright.

Table VIII. Corrosion Rates of Some Mg-Li Alloys

Alloy	Weight Loss Rate After Exposure Time Indicated					
	2 Months		4 Months		8 Months	
	Mg per Dm² per Day	In. per Yr	Mg per Dm² per Day	In. per Yr	Mg per Dm² per Day	In. per Yr
9.5Mg-Li-7 pct Al-1 pct Sn	4.4	0.0036	6.25	0.0051	5.15	0.0042
9.5Mg-Li-7 pct Al-1 pct Mn-0.05 pct Sn	2.35	0.0020	3.8	0.0032	3.6	0.0030
9Mg-Li-5 pct Al-8 pct Zn	1.75	0.0014	1.5	0.0012	1.15	0.0010
AZ31A-H24	1	0.00081	1.05	0.00084	0.9	0.00077

The classification suggested by Mr. Leman for the three types of Mg-Li alloys is a convenient one. Although none of the alloys are yet ready for commercial applications, some may be suitable for special applications where low weight is an important factor. For structural purposes, we believe that the "intermediate strength" alloys of Class 3 offer the greatest promise.

Hydrogen Solubility in Aluminum and Some Aluminum Alloys

by W. R. Opie and N. J. Grant

DISCUSSION, M. Bever presiding

W. Baukloh (*Bengal Engineering College, Howrah, West Bengal, India*)—On p. 1239 of their paper, the authors mention that their results are contrary to evidence presented previously by Baukloh and Oesterlen who observed a minimum in the curves for the solubility of hydrogen in Al-Cu, Al-Si alloys. Attention may be drawn to the publication by Baukloh and Redjali[a] on hydrogen solubility in aluminum with some alloying elements (Co, Cu, Cr, Fe, Th, Ti, and Sn). The effect of copper published by Baukloh and Redjali were found to be similar to the results obtained by the authors.

W. R. Opie and **N. J. Grant** (authors' reply)—We wish to thank Professor Baukloh for the above information which was not available at the time of publication.

[a] W. Baukloh and M. Redjali: *Metallwirtschaft* (1942) 21, pp. 633-688.

Dendritic Crystallization of Alloys

by B. H. Alexander and F. N. Rhines

DISCUSSION, M. Bever presiding

R. W. Ruddle and **A. Cibula** (*British Non-Ferrous Metals Research Association, London, England*)—We have been pleased to see this study of a sadly neglected subject and would like to compliment the authors on an interesting piece of work. In interpreting the results of their investigation the authors suggest that the dendrite arm spacing is governed primarily by heat transfer factors, specifically the ratio "heat of fusion/thermal diffusivity." We think however that, although they have discussed them very fully, the authors have not attached sufficient importance to the effects of concentration gradients in stifling the growth of budding dendrite arms and thus controlling the spacing of those which are able to grow. They state that no direct correlation exists between the arm spacing and freezing range and other constitutional factors, but surely no direct correlation is to be expected since the concentration gradients set up round a growing crystallite and their growth restricting effect should be controlled not only by the freezing range, but also by the slopes of the liquidus and solidus curves and by the rates of diffusion of the solute element in the melt. Unfortunately it is not possible to evaluate the effects of these factors from the information available.

The authors say that: "Because the diffusion of heat and the diffusion of matter obey similar rate laws, it follows that these factors should support each other in their influence on the crystallization of alloys." If the authors mean by this merely that both these effects can restrict the growth of crystals, we are in agreement; but we would point out that both these effects cannot control the rate of growth at the same time. If the growth of an isolated dendrite in an undercooled melt is controlled by heat diffusion, then at first heat must be liberated during solidification faster than it can diffuse into the surrounding liquid; this will result in the setting up of a heat barrier round the growing crystallite, which will then limit the rate of crystal growth. Conversely, if the growth of the dendrite is controlled by the diffusion of metal atoms, a concentration barrier will be produced which will again limit crystal growth; in this case the liberation of heat of fusion must lag behind the extraction of heat by the surrounding melt. Clearly, both factors cannot control the growth of the individual dendrite at the same time.

Our own tentative picture of the mechanism of solidification in pure metals and alloys is as follows. The rate of growth of an isolated crystallite in an undercooled pure metal melt must be limited by the rate of heat diffusion into the liquid, for, as the authors state, concentration gradients are impossible in pure metals. However, the crystals growing in a molten pure metal rarely are isolated in the melt but are normally

attached to the mould wall from which they grow in a columnar manner towards the center of the casting. It follows that the heat liberated during solidification escapes through the solid wall of columnar crystals instead of into the liquid metal (which, except at the onset of solidification, is at or above the freezing point). The rate at which heat flows through the solid wall and consequently the rate of growth of the wall is governed by the rate at which the mould extracts heat.

This mechanism, we think, also must apply to dilute alloys which solidify in a columnar manner and in which the concentration gradients are too small to be effective. As the proportion of solute increases, however, a critical concentration is reached beyond which the growth-restricting effect of the concentration gradient exceeds the limitation on growth imposed by the rate of heat abstraction by the mould. Beyond this critical concentration, therefore, the mould removes more heat than is being liberated by solidification on the existing crystals; when this happens the melt in front of the initial dendrites undercools and crystallization begins at fresh nuclei in the interior of the melt, as has been observed with aluminum alloys.[15] This change in the mechanism controlling the rate of crystal growth is accompanied by a changeover from a columnar to an equiaxial structure. The concentration at which the change takes place is dependent upon the rate of heat abstraction by the mould, a high rate causing the changeover to take place at lower concentrations.

Because of the absence of a heat or concentration barrier in a metal of high purity solidifying in a columnar fashion as described above, the tendency towards dendritic growth is small and depends upon the fact that deposition of metal atoms from the liquid takes place preferentially on certain facets of the growing crystal. The absence of marked dendritic growth in solidifying pure metals is illustrated by the fact that when metals of high purity (e.g., 99.99 pct pure Al) are slush-cast in sand moulds the solid shell remaining in the mould has a smooth surface, whereas a metal of lower purity (e.g., commercially pure aluminum) leaves a shell whose surface is roughened by the tips of protruding dendrites. The development of concentration gradients in the presence of a solute element greatly enhances the tendency to dendritic growth, and the spacing of the dendrite arms presumably increases with increase in the gradients, much as described by the authors on p. 1271. However, as stated above, we do not agree with the authors when they suggest (p. 1272) that the controlling gradients are heat gradients and not concentration gradients. We doubt whether an apparent rough correlation of the kind shown in Table VIII, between the dendrite arm spacings and the ratio "heat of fusion/temperature diffusivity" establishes conclusively that heat gradients control the dendrite spacing, for it is likely that both heat and concentration gradients follow the same general trends with increasing concentration of solute element. In any case, analysis of the figures for the Cu-Ni and Cu-Sn series of alloys shows that the apparent correlations are not statistically significant, the probabilities that the apparent correlations arose by chance both exceeding 0.05; (we are adhering to normal statistical practice in regarding correlations as nonsignificant when the chance probability is greater than 0.05). It should however be stated that when all the figures for the Cu and Ni-base alloys are considered together, a correlation which is on the borderline of significance is found, the chance probability lying between 0.02 and 0.01.

Finally, we wonder whether the authors in their reply could give some further details of the way in which they measured the dendrite spacings of the different alloys. In particular, the description and micrographs in the paper do not make it clear what they regarded as "fully developed arms" and what as "stunted side arms." We should like to draw the authors' attention to a recent paper by Kostron[16] who measured the "cell size" of a large number of aluminum alloys. So far as we can see the cell size measured by Kostron is essentially the dendrite spacing measured by the authors. If this is so, the two sets of measurements are completely at variance for in all cases the cell size measured by Kostron decreases with increase in the amount of alloying element.

A. Hultgren *(K. Tekniska Hogskolan, Valhallaragen, Stockholm, Sweden)*—This paper is a welcome contribution in a field where altogether too little is known and understood with certainty.

In their attempt at assessing a value for the average dendritic spacing at a given distance from the surface of an ingot, the authors often encountered a mixture of types of dendritic branches with different spacings, as pointed out on p. 1268. It is suggested that this may be due to two or more families of dendritic branches forming in succession at the same place.

In an investigation of solidification structures in 1.10 pct C steel ingots of commercial size[17, 18] it was found that the growing skeleton of each columnar crystal was built up of a number of parallel cruciform stems—plates intersecting at right angles—from which, at a later stage, secondary and tertiary rod-shaped branches developed, also in tetragonal directions. The spacing of the stems as seen in the cross-section of a crystal was considerably coarser than that of the rods. Whereas the former spacing appeared to increase by steps from root to tip of a columnar crystal, the latter increased continuously from surface to axis of the ingot, with no distinction between columnar and free crystals. The continuous lines seen here and there in the authors' Fig. 1 may be sections of plate-like branchings of columnar crystals whereas short, more closely spaced lines may be sections of secondary branches. In such case, sections parallel to the surface may be instructive. It is not, of course, suggested that the features described are necessarily present in all alloys with dendritic structure.

In Tables II, III, and V columnar and equiaxed grain sizes are both given. Does this mean that both types of grains were generally present at position (m)?

The authors' detailed picture of the mechanism by which dendritic branching develops appears plausible and, apart from the concept of successively formed idiomorphs, agrees well with an earlier attempt.[19]

Accordingly, and a little differently expressed, it may be said that the dendritic spacing at any point of an alloy crystal is determined mainly by the following two factors: 1—The linear rate of growth of the corner or main stem of the crystal as largely influenced by the degree of undercooling, and 2—the rate of diffusion of the alloying element. In a pure metal heat conductivity would take the place of the second.

As freezing continues inwards and the rate of growth is gradually retarded the shielding effect exerted by the enriched mother liquor gains upon the growing stem and the dendritic spacing is coarsened.

In the many cases where an alloying element was found to coarsen the spacing two factors may act in this direction: 1—Decreased rate of growth owing to lower bulk heat conductivity, and 2—increased diffusion distance and extended shielding effect owing to steeper concentration gradient in the mother liquor; the lower heat conductivity might be expected to have a local effect tending to decrease the spacing but this is probably overshadowed by 1 and 2.

The difference in spacing between primary and secondary branchings at the same place probably results from the cooling rate at any point increasing all the time as the freezing range is passed, the change in composition of the mother liquor meanwhile being of less importance.

The authors' statement that it is only when crystallization proceeds rapidly that dendritic growth is encountered seems to require some qualification.

In steel ingots of large sizes, coarse dendritic free crystals are found in the central region. Their branches have rounded contours, probably resulting from diffusion of alloying elements and surface tension. When

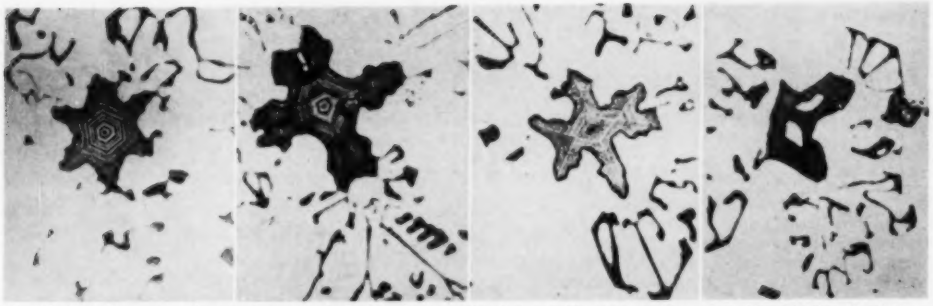

Fig. 11 (left)—Large constituent primary Al-Cu-Fe-Mn phase; smaller dark constituent forms binary eutectic with Al solid solution. The change from the hexagonal mode of growth occurs with depletion of chemical concentration in liquid phase. X500.
Figs. 12 (left center), 13 (right center), and 14 (right)—Influence of the "principal" planes of primary crystallization upon the mode of crystallization of the eutectic phases.
Area reduced approximately 80 pct for reproduction.

the dendritic spacing reaches the same order of magnitude as the size of the crystal, so-called globular structure results. There is a smooth transition between dendritic and globular structure. The latter may be produced in ordinary steel ingots by suitable stirring[15] or, probably, by other methods of inoculation. I should be very much surprised if an idiomorphic δ or γ Fe crystal were produced by crystallization in molten steel.

H. Czyzewski *(University of Illinois, Urbana)*—The writers have given an excellent report of their study in this field, and this discussion is made only as a small contribution to the writers' extensive work. The statement is made in the paper to the effect that the intrusion of a second solid phase, such as appears in richer alloys of eutectic and peritectic types, seems to be without influence upon the dendrite dimensions. This is presumed to be because the establishment of the dendrite pattern precedes the crystallization of the low melting phases.

It is suggested in this discussion that the writers' conclusion holds true for the early stages of crystallization but that in the final stages there would be an influence on dendrite dimensions due to the large chemical-concentration gradient from the solid dendrite to the core of the remaining liquid phase. Because the writers reported mostly on alloys in which the primary crystals were dominant, the effect in the final stages of primary crystallization of the second phase, that is the liquid, on the primary phase was not observed. The schematic representation (Fig. 10 of the paper) shows that there is an effect on mode of crystal growth, and therefore on dendrite dimensions, which is a function of velocity of the growth. The velocity of growth is a function of, among other things, the chemical concentration in the liquid adjoining the growing crystal. The writers conclude that the rate of heat transfer is probably of greater importance than is the rate of material transfer in establishing the dendrite spacing in metal systems. This conclusion is justified by the data only in the cases in which the liquid phase can continue to produce the primary solid phase.

A study of multiphase alloys requires modifications of these conclusions of the writers. For example, Fig. 11 shows a primary crystal identified as the Al-Cu-Fe-Mn phase which occurs in certain cast aluminum alloys of a commercial grade.* The primary crystal shows a series of concentric hexagons of quite regular shape with straight sides and sharp corners. The writers made the statement that "corner rounding" must be expected. This rather common idea is not justified on the basis of Fig. 11. Also, the departure from the hexagonal mode of crystallization in this case does not occur as a function of heat transfer but rather as a function of material transfer and the depletion of the liquid phase. It appears, therefore, that the second phase can exert an influence on the dendrite dimensions.

Conversely, it also may be concluded that the mode of solidification of the primary phase can exert an influence on the mode of solidification of a secondary phase, and therefore on the dimensions of the secondary phase. For example, in Fig. 11 not only the faces of the hexagons are defined but also apparent are the planes passing from the edges of the hexagons through the longitudinal axis of the hexagonal prism. The formation of these "principal" planes of crystallization is subject to interesting speculation. However, these principal planes have an influence on secondary crystallization, in the eutectic in this case, as seen in Figs. 12, 13, and 14.

Perhaps, the following conclusions may be considered. If the rate of material transfer is not greatly affected during the process of primary crystallization, then the rate of heat transfer regulates the dendrite dimensions. However, if the rate of material transfer varies greatly during the process of primary crystallization, then the primary dendrite dimensions and secondary phase dimensions will be affected.

B. H. Alexander and **F. N. Rhines** (authors' reply)—We thank the discussers for their interesting and valuable contributions to this paper. One main point that is brought up repeatedly in the discussion is whether heat flow or material flow is of greater influence on the dendritic growth in alloys. For the reasons given in the paper, we believe that heat flow is the more important, although we recognize that more work must be done before we can be sure.

It should be emphasized that the spacings we measured were what we considered to be the primary arm spacings which are established early in the course of freezing. The formation of secondary and tertiary dendrite arms and their change in shape due to spheroidization was not studied. It is the smaller size of these later generations of arms that determine the "cell-size" measured by Kostron. It is interesting that cell size varies with concentration in a different manner than the arm spacing; we can think of no good explanation for this, although the concentration and temperature would not be expected to be the same during the formation of the later arms as it was when the primary arms formed. We would estimate that the arm spacing in a given alloy is from 2 to 20 times the "cell size."

The grain sizes listed in Tables II, III, and V are the average width of columnar grains or the diameter of equiaxed grains; both types of grain were not found at the same position in an ingot.

References

[15] A. Cibula: *Journal* Inst. of Metals (1949) **76**, p. 321.
[16] H. Kostron: *Ztsch. f. Metallkunde* (1949) **40**, No. 9, p. 321.
[17] *Journal* Iron and Steel Inst. (1929-II) **120**, p. 69.
[18] *Jernk. Annaler* (1930).
[19] Pp. 77-79 of ref. 15.

* The constituent was identified using the procedure in Mondolfo's *Metallography of Aluminum Alloys*. Only one etchant, 30 pct H_2SO_4, revealed the internal structure of this phase as shown in the accompanying micrographs. The etching action produced a relief effect which was deliberately accentuated in photographing and printing.

Technical Note

The Crystal Structure of V_3Co

by Pol Duwez

IN the course of an investigation of the V-Co system, two intermediate phases were found. One of these phases corresponds approximately to the stoichiometric composition VCo and is isomorphous with the sigma phase in the Fe-Cr system.[1] The second phase has the composition V_3Co; its crystal structure is described in the present note.

The alloys were prepared by mixing the two metals in the powder form, pressing a small disk weighing about 5 g at 80,000 psi, and arc melting this disk on a water-cooled copper plate in an atmosphere of pure helium. The details of this technique have been described.[2] The vanadium powder was obtained from Westinghouse Electric Corp., Bloomfield, N. J. This powder is probably of very high purity, since when it is properly sintered or melted in the above-mentioned arc furnace, ductile specimens are obtained. The cobalt powder, from Charles Hardy, Inc., New York, contained 0.5 pct Ni, 0.1 pct Cr, and traces of Si and Fe.

After melting, the V_3Co samples were sealed in evacuated quartz tubes and homogenized for ten days at 800°C. Powder diffraction patterns were obtained with a 14.32 cm diam camera, using $K\alpha$ copper radiation. The patterns were readily indexed on the basis of a primitive cubic lattice with a parameter equal to 4.675A. The density, determined by the immersion method, was 6.71 g per cu cm; hence the number of molecules per unit cell is approximately 1.95; i.e., 2.

At this point, the possibility that the structure might be that of beta tungsten[3] became apparent. The beta tungsten structure is described as follows:

Space group $O^1_h - Pm3n$

2 Co in (a) : 000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$

6 V in (c) : $\frac{1}{4}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{4}0$; $0\frac{1}{2}\frac{1}{4}$; $\frac{3}{4}0\frac{1}{2}$; $\frac{1}{2}\frac{3}{4}0$; $0\frac{1}{2}\frac{3}{4}$

(hhl) reflection present only if $l = 2n$.

Assuming this structure to be the correct one, intensities were computed by means of the usual equation:

$$I \propto p\,|F|^2 \frac{1 + \cos^2 2\theta}{\sin^2\theta \cos\theta}$$

where F is the structure factor, θ the Bragg angle, and p the multiplicity factor. The observed and calculated values of $\sin\theta$ and the intensities are given in Table I. The agreement between the observed and the calculated $\sin\theta$ is good and there are no flagrant discrepancies between the calculated intensities and those estimated visually. The (hhl) reflections for which l is odd are not observed, as required by the space group. In addition, the (410), (430), and (531) reflections are missing as expected, because of the special (a) and (c) positions in O^1_h. However, six reflections—(110), (220), (310), (411), (422), and (510)—which have very weak computed intensities were not observed. For these reflections, the structure factor is proportional to the difference between the scattering factors of the two atoms in the structure. Since the scattering factors of vanadium and cobalt are not very different, these reflections are weak. However, by using $K\alpha$ chromium radiation, whose wavelength is just above the absorption edge of vanadium, the effective scattering factor of vanadium may be decreased by one or two units; consequently the difference between the cobalt and vanadium scattering factors is increased. It was, indeed, found that in a powder pattern taken with chromium $K\alpha$ radiation, the three reflections (110), (220), and (310) were actually present. The three other reflections (411), (422), and (510), with spacings smaller than half the wavelength of chromium $K\alpha$, were obviously not obtainable with chromium radiation.

All the experimental results appear to confirm the beta tungsten structure for V_3Co. In this structure, each cobalt atom is surrounded by twelve vanadium atoms at 2.61A; each vanadium atom is surrounded by two vanadium atoms at 2.34A, four cobalt atoms at 2.61A, and eight vanadium atoms at 2.86A.

Table I. Diffraction Data for V_3Co

hkl	d, A	$\sin^2\theta$ (Observed)	$\sin^2\theta$ (Computed)	Intensity (Observed)	Relative Intensity (Computed)
110*			0.0543		21
200	2.34	0.1079	0.1086	m	425
210	2.08	0.1366	0.1357	s	1000
211	1.90	0.1637	0.1628	s	880
220*			0.2171		3
310*			0.2714		6
222	1.349	0.3262	0.3257	vw	58
320	1.298	0.3534	0.3528	w	195
321	1.247	0.3818	0.3800	m	430
400	1.165	0.4369	0.4342	w	145
411-330			0.4885		2
420	1.044	0.5442	0.5428	w	130
421	1.019	0.5714	0.5699	vw	53
332	0.9962	0.5978	0.5971	w	125
422			0.6514		1
510-431			0.7056		3
520-432	0.8686	0.7864	0.7871	m	320
521	0.8535	0.8143	0.8142	m	290
440	0.8266	0.8683	0.8685	m	300

Quadratic form for copper $K\alpha_1$ radiation:
$\sin^2\theta = 0.02714\ (h^2 + k^2 + l^2)$
s = strong; m = medium; w = weak; vw = very weak.
* Reflection observed in a pattern obtained with chromium $K\alpha$ radiation.

Acknowledgment

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aime NEWS

AIME 1951 Fall Meeting To Be Held In Mexico City

The AIME Fall Meeting, in Mexico City, Oct. 29 to Nov. 3, will be held jointly with the Pan-American Institute of Mining Engineers and Geology, and the Instituto Nacional para la Investigacion de Recursos Minerales. The opening session will be Monday morning, Oct. 29, and technical sessions will be held mornings and afternoons on Tuesday and Wednesday. The Minerals Beneficiation Div. will have a full program, with a somewhat less extensive program scheduled by the Mining, Geology, and Geophysics Div., Industrial Minerals Div., and Mineral Industry Education Div.

Many social functions, luncheons, dinners, sightseeing tours, and technical field trips are being planned. This is a good time of year to save for vacations, and some trips have been planned that extend beyond the meeting dates for those who wish to make the most of their trip across the border. Travel facilities to, and living accommodations in Mexico City are excellent, and the tourist will find much to see and buy. A more complete description of the nontechnical activities of this meeting will appear in the July issue of MINING ENGINEERING. Literature and plans concerning the meeting can be obtained by writing William G. Kane, San Juan de Letran 9, Room 805, Mexico 1, D.F.

Dahl Speaks on Columbia's Flat Mills

I. S. Dahl, vice-president in charge of operations, Columbia Steel Co., San Francisco, was guest speaker at the April 18 meeting of the Western Section, National Open Hearth Steel Committee, ISD, held in Los Angeles. He was introduced by Otto A. Kresse, general superintendent, Torrance Works, Columbia Steel Co., and spoke on the recent cold rolled sheet and tin mill installations at the Pittsburgh, Calif., Works of his company. A three-year record in attendance was set when 140 members and guests were present.

Colleges Must Double Enrollment To Meet Demand for Engineers

According to T. A. Marshall, Jr., executive secretary of the Engineering Manpower Commission of Engineers Joint Council, more than 30,000 engineers must be graduated from the engineering schools each year to staff the national effort to out-design, out-develop, out-produce and out-perform a potential enemy who outnumbers this country's population. To achieve this goal, engineering schools will have to more than double present enrollment for years to come.

An output of 30,000 graduates a year, because of the 50 pct mortality rate, would mean a freshman enrollment of 60,000, or 10 pct of the annual male high school output. The doubt expressed by educators that the combined factors of aptitude, ability, interest, etc. could be found in this large requirement leads to the conclusion that an inexhaustible supply of engineering talent cannot be developed. It is estimated that there will still be an accumulated shortage of 40,000 engineers by 1954.

Engineering Manpower Commission is trying to emphasize to high school principals, counselors, and students the critical shortage of engineers in all fields. The U. S. Bureau of Labor Statistics states: "Industry has been using an increasing proportion of engineers in relation to total number of workers employed. As a result, the number of engineers employed has increased rapidly and would continue to grow in the long run, even under peacetime conditions. Additional engineers will be needed for defense mobilization. Despite record graduations over the past few years, industry is seeking additional personnel, particularly for the defense program. The number of graduates is expected to drop, mainly because veteran enrollments have declined. Those now planning to enter engineering schools should find good employment prospects when they finish their courses."

When notifying AIME headquarters of a change of address, or of company position or affiliation, *please mention the Branch of the Institute to which you belong—Mining, Metals, or Petroleum.* This will make for a more expeditious handling of the change and will facilitate the preparation of various reports.

Divisions Nominate 1952 Officers

Institute of Metals Div.: Chairman, Walter A. Dean; Sr. Vice-Chairman, Morris Cohen; Vice-Chairman, Jack Scaff; Secretary, Ernest Kirkendall; Executive Committee (until 1955), George P. Halliwell, Oscar T. Marzke, and William E. Mahin.

Iron and Steel Div.: Chairman, K. C. McCutcheon; Vice-Chairmen, J. B. Austin, E. K. Miller, and T. J. McLoughlin; Executive Committee (until 1955), Walter Carroll, H. M. Griffith, and J. S. Marsh.

Extractive Metallurgy Div.: Chairman, T. D. Jones; Chairman Elect, R. R. McNaughton; Secretary, Ernest Kirkendall; Executive Committee (until 1955), J. C. Kinnear, Jr., and John D. Sullivan.

Mineral Industry Education Div.: Chairman, Harry H. Power; Vice-Chairman, J. R. Van Pelt; Past Chairman, Allison Butts; Executive Committee (until 1955), C. J. Christiensen, C. S. Crouse, and E. M. Thomas.

Minerals Beneficiation Div.: Chairman, E. H. Crabtree, Jr.; Associate Chairman, Donald W. Scott; Regional Vice-Chairmen, S. D. Michaelson, and Will Mitchell, Jr.; Secretary-Treasurer, William Stephenson.

Mineral Economics Div.: Chairman, Evan Just; Vice-Chairmen, Granville Borden, J. K. Richardson, S. H. Williston; Secretary-Treasurer, Allan Matthews; Executive Committee, R. D. Parks, M. D. Harbaugh, G. H. Cady. To replace Evan Just on Exec. Comm.—S. G. Lasky.

Haider and Fletcher Head 1952 AIME Nominations Slate

Clayton G. Ball, Chairman of the Nominating Committee, has announced nominations for President, President-elect, Vice-Presidents, and Directors for 1952. As provided in Art. IX, Sec. 2, of the bylaws, 25 members or associate members may sign and transmit to the Secretary's office prior to Sept. 1 "any complete or partial ticket of nominees," should they wish other candidates to be considered.

In such instance, a letter ballot will be forwarded to all members in good standing in the United States, Canada, and Mexico, tabulating both the official ballot and any supplementary nominations. If no supplementary nominations are thus received, no letter ballot will be printed, and nominees on the official ballot shall be declared duly elected at the meeting of the Board of Directors or the Executive Committee in November.

M. L. HAIDER
President, 1952

ANDREW FLETCHER
President, 1953

Vice-Presidents

O. B. J. FRASER

J. B. MORROW

For President

Michael Lawrence Haider was born in Mandan, N. Dak. in 1904. He attended the University of Southern California and Stanford University from which he graduated in 1927 with a B.A. degree in chemistry. After graduation, he was employed by the Pacific Portland Cement Co. and later entered the petroleum industry with the Pan-American Petroleum Co. from which he was transferred to the Richfield Oil Co. In 1929, he became affiliated with the Carter Oil Co. Mr. Haider joined the Standard Oil Development Co. in 1938 as manager of the production engineering and research dept. In 1945 he was transferred to the producing dept. of Jersey Standard Oil Co. in the position of executive assistant and was responsible for various foreign operating affiliates. In 1946 he was transferred to Imperial Oil Ltd., Canadian affiliate, with headquarters in Toronto, his current residence. In 1948 Mr. Haider was elected to the board of directors of Imperial and in 1950 became a vice-president. He is currently responsible for the purchasing and transportation departments. Mr. Haider became a member of the Board of Directors of AIME this year. For several years he served as Chairman of the Publications Committee of the Petroleum Div., was Chairman of that Division in 1945, and has been active on numerous committees of the Institute.

For President-Elect

Andrew Fletcher, president of St. Joseph Lead Co., has been nominated for the Presidency of AIME in 1953. Mr. Fletcher, who was born in 1895 in New York City, was educated at Hill School and the Sheffield Scientific School, Yale University, where he received a Ph.B. in mechanical engineering. In 1949 the University of Missouri conferred upon him an honorary degree of Doctor of Engineering. In addition to being president of St. Joseph Lead Co., he is also president of Mine La Motte Corp., and Bonne Terre Farming & Cattle Co. He is vice-president of Missouri-Illinois R. R. Co. and director of the American-Hawaiian Steamship Co. He has been on the Board of AIME for many years, and has been Treasurer since 1944.

For Vice-Presidents

Oliver B. J. Fraser, assistant manager of the development and research div. of International Nickel Co., New York, has been an AIME member and a highly active one, since 1918. He is a past Chairman of the New York Section and has served on the following AIME committees: Ways and Means (1945-46); MINING AND METALLURGY (as chairman); President's Advisory (1947-48); Nominations for 1951 AIME Officers (as chairman); Auxiliary Publications Committee, Institute of Metals Div. (as chairman), and on the Program Committee, IMD. He is the author of many outstanding publications and the AIME has published many of his technical papers. Mr. Fraser was born at Brockville, Ont., in 1895, and received the degree of B.Sc. at Queen's University.

James Bain Morrow, vice-president, retired, of Pittsburgh Consolidated Coal Co., was born in Halifax, Nova Scotia in 1886 and studied mining engineering at Dalhousie University. No better summary of Mr. Morrow's qualifications could be given than to quote from the citation read on presentation of the Erskine Ramsay Gold Medal at the AIME Annual Meeting in St. Louis last February: "As an engineer and scientist, Mr. Morrow has served the coal mining industry with distinction. As an executive, he has invariably presided with tact, judgment, and success. . . . In his active life, he has always found time to devote to young engineers, acting as an inspiration to them, and thereby enriching the industry with young blood." He has figured prominently on many committees of the AIME; and as Chairman, Vice-Chairman, and a member of the Executive Committee of the Coal Div.,

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T. L. JOSEPH

C. E. REISTLE, JR.

he has taken a leading part in its activities. Many of his technical papers on the cleaning, sampling, and preparation of coal have been published by the Institute. In 1944 he received the Percy Nicholls Award.

For Directors

C. Harry Benedict has been nominated Director of AIME for a three-year term beginning February 1952. He previously served as Director from 1945 to 1950 and as Vice-President from 1948 to 1950. Mr. Benedict was born at Pittsburgh in 1876 and graduated from Cornell University in 1897. Immediately after graduation he became affiliated with Calumet & Hecla Consolidated Copper Co. He retired from active duty with this company in 1948. So much has been written about the famous ammonia leaching process, which Mr. Benedict developed, for recovery of copper from waste sand (tailing), that it is unnecessary to repeat an account of this achievement. Although Mr. Benedict has retired from "active" services with his company, he still continues his activities on behalf of the Institute and various other organizations, and is also writing a history of the Calumet & Hecla Consolidated Copper Co., which will be published late this year.

Russell B. Caples has been nominated as Director of AIME for the term 1952 to 1955. He was born in Glasgow, Mo. in 1888 and graduated from the Missouri School of Mines in 1910, where he received an honorary degree of Doctor of Engineering in 1948. Mr. Caples started his professional career with the Federal Mining & Smelting Co. in the Coeur d'Alene district of Idaho and shortly thereafter entered the employ of the Anaconda Copper Mining Co. He was first employed in the testing dept. of the Anaconda Reduction Works, working in collaboration with Messrs. Frederick Laist, F. F. Frick, and James O. Elton in the development of the electrolytic zinc process during 1914 to 1916 as well as the basic process for the Anaconda phosphate plant. In 1918 he became superintendent of the Great Falls, Mont., plant and was made manager in 1941. He has served on various committees of the Extractive Metallurgy Div. of the Institute, including the Executive Committee and its Committees on Lead and Zinc, and Pyrometallurgy. He is also a member of the Advisory Committee on Zinc of the Defense Minerals Administration.

Theodore Benton Counselman has been nominated Director of AIME for a three-year term beginning February 1952. He was born in New York in 1889, and graduated from Columbia University with the degree of engineer of mines. After a short apprenticeship with what later became Texas Gulf Sulphur, and with Inspiration, he got into ore dressing under the late John M. Callow. He followed this star to Greene Cananea, back to Arizona Copper Co. in Morenci, to Miami, and then went with D. C. Jackling on the first of the taconite ventures, the Mesabi Iron Co. After eight years with that company, he turned from operation to equipment sales and joined Dorr Co. where he became manager of their central div. in charge of the Chicago office. He is now in the Stamford, Conn. office.

Mr. Counselman joined the AIME in 1914 and since then has been constantly active in its behalf. He was Chairman of the Chicago Section, Chairman of the Milling Methods Committee, and was largely instrumental in the later transmutation of that committee into the present Minerals Beneficiation Div. He was chairman of the committee which raised the fund for the Richards Award. He is currently a member of the Richards Award Committee and has been a member of the Douglas Medal Committee. At one time he was Vice-Chairman of the Blast Furnace Coke Oven and Raw Materials Committee of the Iron and Steel Div. After coming to New York, he became Chairman of the New York Section, thus having the distinction of being past Chairman of two AIME Sections. He served for several years on the Admissions Committee; and when the Council of Section Delegates was reorganized on a more permanent basis in 1950, he became the first Secretary of the Council. He is currently Chairman of the national Membership Committee.

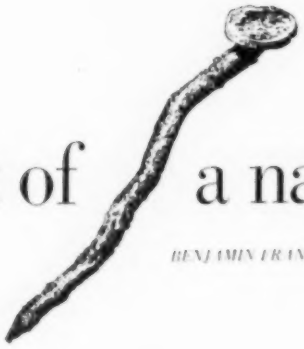
Thomas L. Joseph has been nominated Director of AIME to serve from 1952 to 1955. As Chairman of the Iron and Steel Div., he is currently a member of the Board of Directors, ex officio. Mr. Joseph was born in Adamsville, Utah, in 1894 and graduated in 1917 from the University of Utah with an M.A. degree. He was with the Ordnance Dept. of the U.S. Army during World War I, and later employed by the U. S. Bureau of Mines at its North Central Experiment Station in Minneapolis. In 1936, Mr. Joseph resigned from the Bureau of Mines to become head of the dept. of metallurgy, Minnesota School of Mines and Metallurgy, where he is now assistant dean of the Institute of Technology. Mr. Joseph is the author of numerous papers on iron ore, sinter, metallurgical coke, and various phases of the blast-furnace process. During World War II he was a member of the War Metallurgy Committee on which he planned and supervised a project designed to increase the output and efficiency of blast furnaces. In 1927 Mr. Joseph was the recipient of the J. E. Johnson, Jr. Award; he received the Richard W. Hunt Medal and Prize in 1937, and was Howe Lecturer for 1946.

Carl Ernest Reistle, Jr. has been nominated Director of AIME for a three-year term beginning February 1952. He was born at Denver in 1901 and graduated from the University of Oklahoma in 1922 with a B.S. in chemical engineering. Following graduation he worked as a petroleum chemist for the U. S. Bureau of Mines at Bartlesville, Okla. and later at Laramie, Wyo., where he was also an honorary member of the faculty at the University of Wyoming. He returned to Bartlesville in 1929 and remained with the Bureau of Mines until 1933 when he became Chairman of the East Texas Engineering Assn. It was through the cooperative efforts of member companies of this association that many of the conservation rules and regulations of the Railroad Commission were perfected. In 1936 Mr. Reistle joined Humble Oil & Refining Co., in 1948 was elected a member of the board of that company and is at present director in charge of the production dept.

During World War II, Mr. Reistle served as technical adviser for District III of the Petroleum Administration for War and also served the Office of Price Administration as national vice-chairman of the Oil Industry Advisory Committee. He is the author of numerous papers, several of which have been published by AIME, and has been issued a number of patents.

"For the want of a nail the shoe was lost,
For the want of a shoe the horse was lost,
For the want of a horse the rider was lost,
For the want of a rider the battle was lost,
For the want of a battle the Kingdom was lost . . .

and all for want of a nail"



BENJAMIN FRANKLIN, "Poor Richard," 1758

The fate of nations often hangs on little things. Take this rusty old nail. It symbolizes thousands of tons of worn-out machines and broken parts lying useless in our plants, factories, farms, and homes—scrap steel desperately needed today by our steel mills.

You can help make this nail, and all the other scrap you can collect, go to work again . . . in new steel for ships, tanks, and guns required for defense purposes.

So survey your plant now for every last bit of scrap. Then get it to your scrap dealer promptly. This will not only help assure the nation of the arms needed to preserve our freedom, but it will also mean more steel for your own products tomorrow.

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Personals

GEORGE W. WUNDER

W. P. GETTY

F. M. JARDINE

George W. Wunder, plant manager of National Lead Co.'s MacIntyre development, has been appointed plant manager of the AEC's Feed Materials Production Center planned for construction near Cincinnati. National Lead Co. is contract-operator of the plant.

W. P. Getty has been appointed assistant to the vice-president, operations, Jones & Laughlin Steel Corp., Pittsburgh. He had been assistant general manager of raw materials.

F. M. Jardine, metallurgical engineer, has become field manager for the Round Mountain Gold Dredging Corp., Round Mountain, Nev.

Carl F. Clausen, manager of manufacturing research for the Portland Cement Assn. of Chicago, has been named consultant in the Building Materials Div. of NPA's facilities and construction bureau.

Frank E. Koebel is now associated with the Van Itallie Corp., New York.

Max Hansen has been named assistant chairman of the metals dept. of Armour Research Foundation of Illinois Institute of Technology, Chicago.

Dudley H. Rowland, formerly research associate at the laboratory of the research and technology dept., U. S. Steel Co., has been promoted to assistant to the manager. **Shadburn Marshall,** formerly research associate on the research and development staff, has been transferred to the laboratory to supervise research programs in process metallurgy. **Robert L. Stephenson,** who had been chief metallurgist at the Duquesne works, has been appointed research associate and will supervise research concerning blast furnace developments.

Clinton H .Crane has been reelected chairman of the board, St. Joseph Lead Co., New York. **Andrew Fletcher** was reelected president; **C. Merril Chapin, Jr.,** vice-president; **Francis Cameron,** vice-president; **George I. Brigden,** vice-president and treasurer; and **Felix E. Wormser,** vice-president. **Charles R. Ince** and **Rene J. Mechin** have been elected vice-presidents.

Charles A. J. Schulte has been promoted to assistant plant metallurgist, Vanadium Corp. of America, Niagara div., Niagara Falls, N. Y.

Charles G. Purnell is now manager, process industries section, U. S. Steel Co., Pittsburgh.

Frederic H. Harf is a trainee in metallurgical engineering with Westinghouse Electric Corp., Wilkinsburg, Pa.

Charles H. Parcells has been awarded the first International Nickel Co. graduate fellowship in metallurgical engineering at Illinois Institute of Technology. He has been an instructor in metallurgy at the Illinois Institute for the past year.

Herbert C. McCollum is now consulting engineer with McCollum & Associates, Chicago.

Verne H. Schnee is located with the Metallurgical Advisory Board, Washington, D. C.

Heyward M. Wharton is working on an assignment for the Bethlehem Steel Co. in Brazil.

Gilbert Soler has been made supervisor, research associates, of the research and development staff in the research and technology dept. of U. S. Steel Corp. **John H. Richards** has been promoted to the research and development staff.

Willis H. Wamsley has been made assistant mine superintendent, Climax Molybdenum Co., Climax, Colo.

R. G. Swift has returned as assistant furnace superintendent for the Tin Processing Corp., Texas City, Texas. He had been working for General Electric Co. on an AEC project at Richland, Wash.

Julian Glasser, physical chemist at Armour Research Foundation of Illinois Institute of Technology, has been named technical aide on titanium and zirconium research in a new metallurgical unit of the National Research Council.

Kenneth E. Campbell has joined Battelle Memorial Institute as a research engineer.

Howard D. Crawford has resigned as chief chemist, Phelps-Dodge Corp., United Verde Branch, to accept the position of safety supervisor, Apache Powder Co., Benson, Ariz.

Linton D. Bylund, Reynolds Metals Co., has been transferred from Richmond, Va., to Adrian, Mich.

E. L. La Grelius is now associated with the Alloy Precision Castings Co., Cleveland.

Felix E. Wormser has been reelected president of the Lead Industries Assn. **J. A. Martino** and **K. C. Brownell** were reelected vice-presidents and **R. L. Ziegfield** was reappointed secretary-treasurer.

Willis McG. Peirce, 1951 President of AIME, is now located at the New York office of N. J. Zinc Co. Mr. Peirce has previously been at Palmerton, Pa.

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Name _____

Address _____

City, Zone, State _____

(JM7)

William Hegmann, Jr., metallurgical engineer, has joined the Athletic Mining & Smelting Co., Fort Smith, Ark.

John Chipman, head, dept. of metallurgy, Massachusetts Institute of Technology, has been named president of the ASM. **Ralph L. Dowdell**, head, dept. of metallurgy, University of Minnesota, has been named treasurer and **George A. Roberts**, chief metallurgist, Vanadium-Alloys Steel Corp., trustee.

L. A. Hamilton is export manager for the cooling equipment div., Binks Mfg. Co., Newark, N. J.

Robert L. Pettibone has joined Eaton Mfg. Co., Detroit, as powder metallurgist.

Roger D. Moeller has resigned from the staff of the Los Alamos Scientific Laboratory, Los Alamos, N. Mex. He is now with the atomic energy research dept. of North American Aviation, Inc., Downey, Calif.

Thomas G. Foulkes has been made assistant chief metallurgist, Bethlehem Steel Co., Bethlehem, Pa.

William J. C. Lewis is now associated with the Canadian Westinghouse Co., Hamilton, Ont., as assistant foundry metallurgist. He was formerly with the Canadian Furnace Co., Ltd., Port Colborne, Ont.

Harry L. Watson, Jr. has resigned from the Midvale Co., Philadelphia, and is now with the Catalytic Construction Co., Philadelphia, as job engineer.

Norman P. Pinto, senior engineer, research dept., Rem-Cru Titanium, Inc., has been transferred from Bridgeport, Conn., to Midland, Pa.

Bernard S. Lement is in the metallurgical dept. at Massachusetts Institute of Technology, Cambridge. He was formerly at the University of Notre Dame.

Stanley Walter Madsen has joined Metallurg Inc., New York.

Rex F. Pearce has resigned from the Rhokana Corp., Northern Rhodesia, and has joined South African Cyanamid Pty. Ltd., Johannesburg, South Africa.

Dale C. Matthews is now general superintendent, AEC contract, Galigher Co., Monticello, Utah.

W. Clark Mason has joined the Oliver United Filters, Inc., Oakland, as sales engineer.

J. Verdussen, Union Miniere du Haut-Katanga, Brussels, Belgium, was recently appointed a representative of Engineers' Joint Council.

Robert F. Domagala has been promoted to assistant metallurgist by the Armour Research Foundation, Chicago.

Hugh H. Bein recently returned from the Philippines and is now employed by the Atomic Energy Commission as field metallurgist with headquarters in Grand Junction, Colo.

John A. Watts is now metallurgical engineer with the American Zinc Co. of Illinois, East St. Louis, Ill.

Charles L. Carlson has recently joined the metallurgical application section of the materials engineering dept., Westinghouse Electric Corp., East Pittsburgh.

Annual Meeting Paper Deadline

Sept. 15, 1951 is the deadline for all Institute of Metals Division papers for the 1952 New York Annual Meeting and the deadline for all Iron and Steel Division and Extractive Metallurgy Division papers to be prepublished.

Ulysses H. Berthier (Member 1916) died on March 1. Mr. Berthier was born at Mexico City in 1893. He came to the United States and attended Spring Hill College, Mobile, Ala. and in 1916 graduated with the degree of E.M. from the Colorado School of Mines, Golden. For a short time he was employed by the International Smelting Co., Tooele. In 1917 he joined the Cia. Minera Paloma y Cabrillas, S. A. Higueras, Coah. as engineer. This firm was a subsidiary of the Penoles Co. and in 1919 he was in charge of the parting plant at the Monterrey smelter for the Penoles Co. He was made assistant superintendent and then refinery superintendent for various smelters owned by the Penoles Co. At the time of his death he was residing at Monterrey, Mexico.

Philip L. Edwards (Member 1945) died on March 17. Mr. Edwards had been associated with the Raybestos-Manhattan, Inc., Manhattan Rubber Div. for 32 years. Born in Alden, Iowa on Nov. 12, 1896, he graduated from the Iowa State College, Ames, in 1917 with the degree of B.S. in agricultural engineering. For one year he was employed by the Goodyear Tire & Rubber Co., Akron and in 1919 joined Raybestos-Manhattan, Inc., Passaic. For five years he was located in the Chicago office and in 1924 did sales work in Indiana and adjacent territory. He was made office manager in 1929 and in 1934 became manager, products div., Pittsburgh. Later he became assistant manager of the central district.

Charles Engelhard (Member 1935), president of the Irvington Smelting & Refining Works, Irvington, N. J., died in December 1950. Mr. Engelhard was born in Germany. He came to the United States and in 1891 was engaged in the commercial development of the platinum industry. In 1904 he joined Baker & Co., Inc., Newark, N. J. as general manager and treasurer. At the same time he was associated with the Irvington Smelting & Refining Works, Hanovia Chemical & Mfg. Co., and was also president of Charles Engelhard, Inc.

NECROLOGY

Date Elected	Name	Date of Death
1937	H. H. Burhans	Unknown
1934	James L. Leonard	May 5, 1951
1949	C. O. Penney, Jr.	November 1950
1944	Joseph Pursglove, Sr.	Apr. 24, 1951
1889	F. F. Sharpless	Apr. 11, 1951
1945	Ray E. Tower	Unknown

Proposed for Membership

Metals Branch AIME

Total AIME membership on May 31 was 17,002; in addition 2379 Student Associates were enrolled.

ADMISSIONS COMMITTEE

Thomas G. Moore, Chairman; Carroll A. Garner, Vice-Chairman; George B. Corless, F. W. Hanson, Albert J. Phillips, Lloyd C. Gibson, R. D. Mollison, John T. Sherman. Alternates: A. C. Brinker, H. W. Hitzrot, Plato Melozemoff, Ivan Given, T. D. Jones, and W. H. Farrand.

Institute members are urged to review this list as soon as the issue is received and immediately to wire the Secretary's office, night message collect, if objection is offered to the admission of any applicant. Details of the objection should follow by mail. The Institute desires to extend its privileges to every person to whom it can be of service but does not desire to admit persons unless they are qualified. Objections must be received before the 30th of the month on Metals and Mining Branches.

In the following list C/S means change of status; R, reinstatement; M, Member; J, Junior Member; A, Associate Member; S, Student Associate.

Alabama
Tuscumbia—English, John Benjamin (M)

Arizona
Hayden—Downey, Frank J. (M)

California
Los Angeles—Wilson, John Elmer (M)

Connecticut
Manchester—Bergin, Edward R. (M)
Meriden—Brown, Douglas M. (E)
Waterbury—Scala, Eraldus (J)

Florida
Sarasota—Silvertooth, Lynn L., Jr. (J) (C/S—S-J)

Illinois
Chicago—Aufderhaar, Herman C. (M) (R, C/S—A-M), Coleman, Lee H. (M), Kessler, Harold D. (J), Levin, Sam S. (M), McCurdy, Ray J. (M), Mohr, Louis E. (A), Naismith, Harry (A), Pintchuk, Norman S. (J) (C/S—S-J)
Oaklawn—McPherson, Donald J. (J) (C/S—S-J)
Olympia Fields—Rys, Frederick Wm. (M)

Indiana
Gary—Odom, Wilfred L. (M)
Highland—Hilkert, Ralph V. (R) (M)

Massachusetts
Dorchester—Seigle, Leslie L. (M)
Worcester—Danec, Joseph C. (M) (C/S—A-M)

Michigan
Allen Park—Collison, William H. (M)
Detroit—Bogart, Harold Nelson (M), Semchyshen, Marion (M) (C/S—A-M)
Midland—Watters, Donald W. (M) (C/S—J-M)

Minnesota
Hibbing—Bloomquist, James W. (A)

New Jersey
Fords—LaVelle, Donald L. (M) (C/S—J-M)

New York
Brooklyn—Anderson, John N. (J)
Buffalo—Anderson, Augustus E., Jr. (A), Furnes, Edward J. (A)
New York—Adler, A. G. (JM) (C/S—S-JM), Herasymenko, P. (M), Stone, Louis Pyle (J) (C/S—S-J)
Seaford—MacKenzie James T., Jr. (M) (C/S—A-M)

Ohio
Chagrin Falls—March, George (A)
Cleveland—Whittenberger, Edmond J. (J) (R, C/S—S-J)
Cleveland Heights—Macey, Herbert G. (A)
Middletown—Marshall, William E. (M)

Oregon
Albany—Anabie, Wallace Edw. (J)

Pennsylvania
Lansdale—Weand, Arthur R. (J)
Pittsburgh—Murray, John S., Jr. (J) (C/S—S-J), Wandrisco, J. M. (M) (C/S—J-M)

Tennessee
Oak Ridge—Cremer, George D. (M) (C/S—A-M)

Texas
Houston—Dill, Herbert Clyde (M)

Utah
Tooele—Jacky, Howard W. (M), Long, Robert E. (M)

Washington
Vancouver—Mehl, Fred G. (M) (R, C/S—J-M)

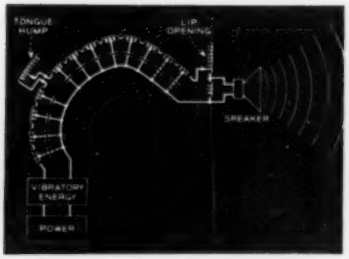
Australia
Tasmania—Whitford, Hedley N. (M)

Egypt
Cairo—Taha, Yousef Ismail (M)

Japan
Tokyo—Tsutsumi, Eizaburo (M)

Mexico
Mexico City—Covacevich, Nick S. (M)
Mexico D.F.—Roldan, G. David (A)
Piedras Negras—Bermea, Arturo (M)

It tells how you talk



The machine at the left is saying "Ah!" It's the new electrical vocal system developed at Bell Laboratories. Top sketch shows human vocal system also saying "Ah!" The electrical model is sketched below it. Energy source at bottom of "tract" can emit a buzz sound, like vocal cord tone, or the hiss sound of a whisper.

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Electric waves copy those of the vocal cords, electric elements simulate the vocal tract, and, by adjustments, vowels and consonants are produced at pitches imitating a man's or woman's voice.

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This is another step in the research at Bell Telephone Laboratories which pioneered the exact knowledge of speech. Past work in the field is important in today's fine telephone service. A still deeper understanding of speech is essential in planning for tomorrow.

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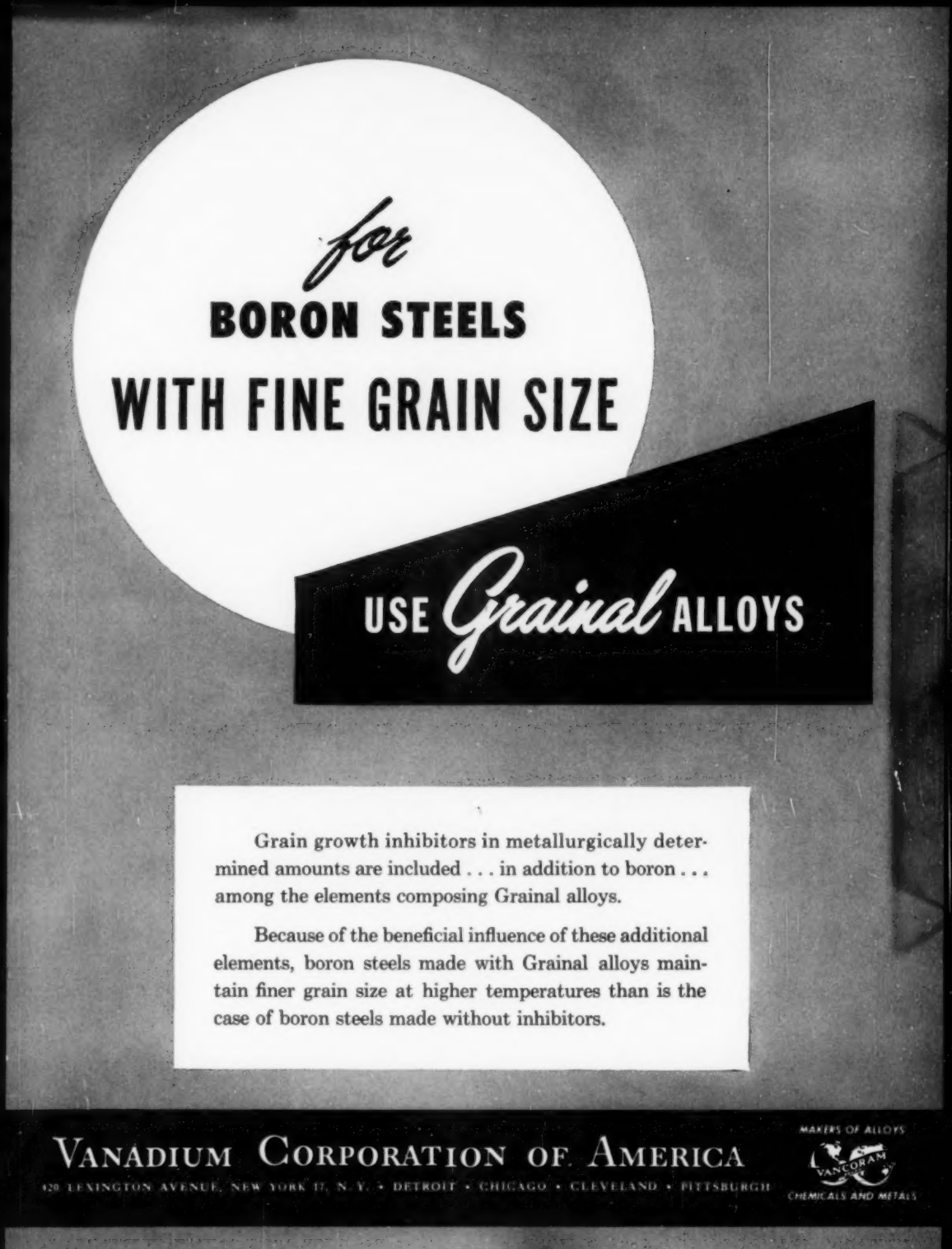

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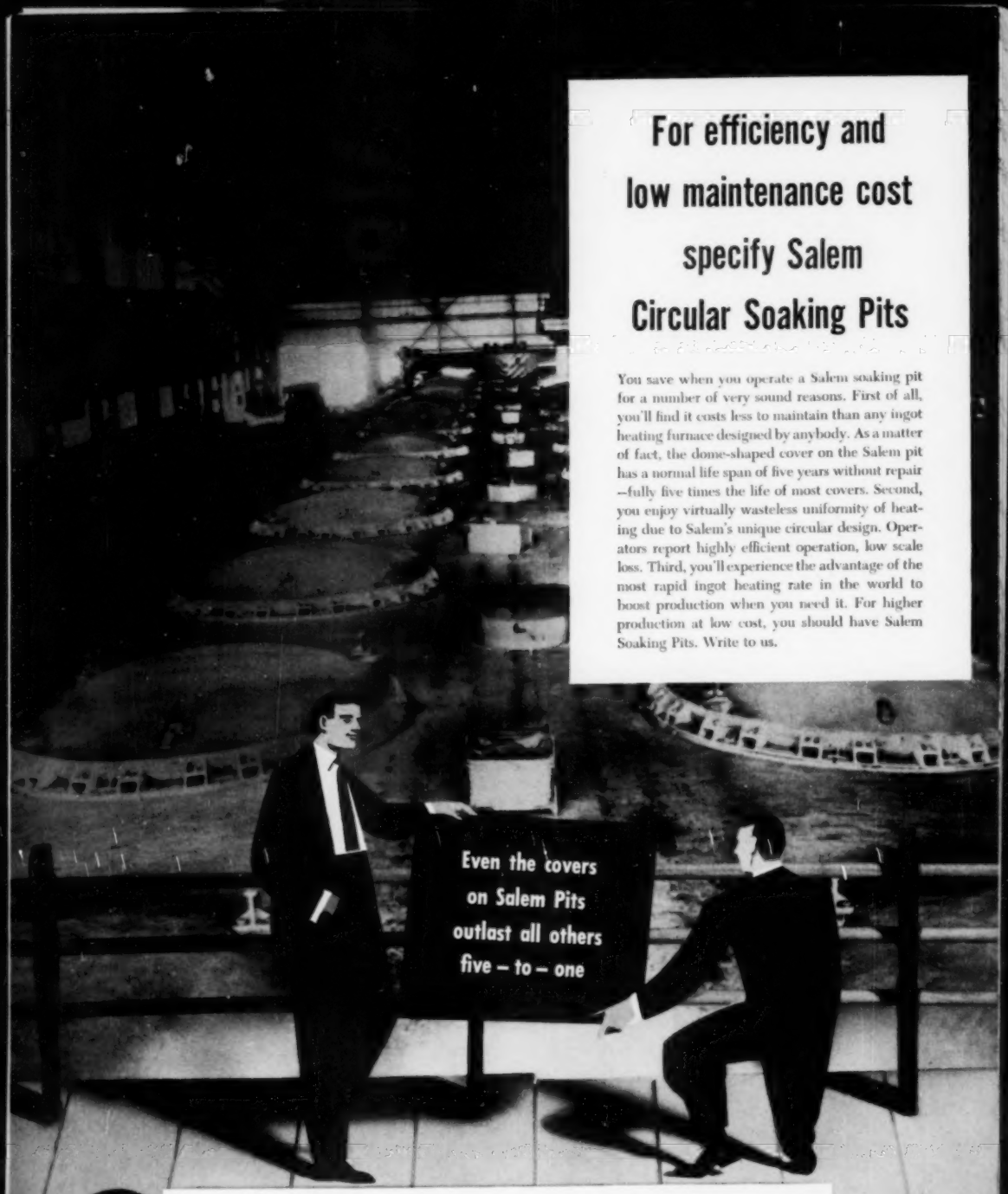

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